126

December 1958 Pages 813 - 888

The Journal *of the* Society of Dyers and Colourists

Volume 74 Number 12

CONTENTS

THE SOCIETY OF DYERS AND COLOURISTS
DEAN HOUSE PICCADILLY BRADFORD YORKSHIRE

Record of Proceedings of the Perkin Centenary

held in London in May 1956

Arrangements have been concluded whereby the proceedings of the Perkin Centenary are being published by Pergamon Press Limited, of 4 Fitzroy Square, London W.1, at the price of 2 gns. per volume. The Publishers have undertaken to donate to the Perkin Centenary Trust a generous proportion of the profits arising out of sales of this volume.

In addition to the four Perkin Lectures which formed such an important part of the Centenary Celebration, the volume contains a Foreword by Sir Robert Robinson F.R.S. and the speeches given at the Centenary Banquet. It also includes a list of the contributors to the Perkin Centenary Fund (now the Trust).

Subscribers to the Perkin Centenary Fund and Sponsoring Bodies should address their orders to the General Secretary at the Society's Offices, and others should make application direct to the Publishers.

The Journal of the Society of Dyers and Colourists

(Subscription rates for non-members £5 5s 0d per annum, post free)
(Abstracts section only printed on one side of paper—£2 0s 0d per annum)

NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc, should consult pages 1–7 of the January 1958 and pages 509–516 of the July 1958 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Fluorescent Brightening Agents — *D. A. W. Adams*

Some Chemical Foundations of Fast Colour Printing — *F. R. Alsberg, W. Clarke, and A. S. Fern*

The Determination of Damage to Wool Fibres — *J. C. Brown*

The Life and Times of Peter Griess — *W. H. Cliffe*

Some Experiments on the Effect of Dye, Fibre, and Atmosphere on Light Fastness — *G. Schwen and G. Schmidt*

COMMUNICATION

A Study of the Spectral Dependence of the Fading of Dyed Textiles — *R. E. Bedford*

EXPLANATORY PAPER ON MODERN THEORY

Surface Activity, Solution, and Adsorption — *C. H. Giles*

FORTHCOMING MEETINGS OF THE SOCIETY

Tuesday, 6th January 1959

LONDON SECTION. *To Blend or not to Blend—That is the Question.* Professor J. B. Speakman, D.Sc., F.R.I.C., F.T.I. (Leeds University). (Joint meeting with the London Section of the Textile Institute.) Chemical Society, Burlington House, **London W.1.** 6.30 p.m.

Thursday, 8th January 1959

MANCHESTER SECTION. *Colour—in Theory and in Practice.* E. Atherton, Esq., B.Sc., Ph.D., F.Inst.P. (Imperial Chemical Industries Ltd., Dyestuffs Division, Blackley). (Joint meeting with the North Lancashire Section of the Royal Institute of Chemistry.) Technical College, **Blackburn.** 7.30 p.m.

WEST RIDING SECTION. *New Levelling Agents in Acid and Direct Dyebaths.* G. H. Lister, Esq., B.Sc., Ph.D. (Sandoz Products Ltd.). Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 9th January 1959

LONDON SECTION. *Optical Brightening Agents in Action.* J. L. Ashworth, Esq., B.Sc., Ph.D., H. B. Mann, Esq., T. H. Morton, Esq., M.Sc., Ph.D., F.S.D.C., F.T.I. (Courtaulds Ltd., Textile Research Laboratory, Bocking.) The Royal Society, Burlington House, **London, W.1.** 6 p.m.

Tuesday, 13th January 1959

NORTHERN IRELAND SECTION. *Some Observations in the Uses of Synthetic Resin Products and Chemical Reactants to Cellulosic Materials.* F. Sloan, Esq., M.Sc. (Kirkpatrick Bros. Ltd.). Grosvenor Rooms, **Belfast.** 7.30 p.m.

SCOTTISH SECTION. *Dyeing Unions Containing Acrylic Fibres.* B. Kramrisch, Esq., F.R.I.C., F.T.I., F.S.D.C. (Ciba Clayton Ltd.). St. Enoch Hotel, **Glasgow.** 7.15 p.m.

Thursday, 15th January 1959

MANCHESTER JUNIOR BRANCH. *Management.* Prof. R. W. Revans. Room J/B 16 — Chemical Engineering Building (Jackson Street), College of Science and Technology, **Manchester.** 4.30 p.m.

Friday, 16th January 1959

MANCHESTER SECTION. *The Degradation of Chemically Modified Celluloses by Alkali.* Dr. W. M. Corbett (British Rayon Research Association). The Textile Institute, 10 Blackfriars Street, **Manchester.** 7 p.m.

Monday, 19th January 1959

HUDDERSFIELD SECTION. Title to be announced later. Professor J. B. Speakman, D.Sc., F.R.I.C., F.T.I., F.S.D.C. (Joint meeting with the Huddersfield Textile Society.) Large Hall, Technical College, **Huddersfield.** 7.30 p.m.

Tuesday, 20th January 1959

SCOTTISH JUNIOR BRANCH. *Variables in the Cold Batchwise Dyeing of Reactive Dyes.* I. H. Burnett, Esq., B.Sc. (Imperial Chemical Industries Ltd.). The Loch Lomond Hotel, **Balloch.** 7.30 p.m.

Wednesday, 21st January 1959

MIDLANDS SECTION. *The Solubility of Wool Dyes . . . Assessment and Practical Significance.* W. Beal, Esq., B.Sc. College of Technology, **Leicester.** 7 p.m.

Thursday, 22nd January 1959

WEST RIDING SECTION. *Some Aspects of Reactive Dyes.* Dr. J. Wegmann. (Ciba Ltd., Basle). Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 23rd January 1959

LONDON SECTION. Annual Dinner and Dance. Waldorf Hotel, **London, W.C.2.** 7 p.m. for 7.30 p.m.

WEST RIDING SECTION. Ladies Evening. Victoria Hotel, Bridge Street, **Bradford.**

Monday, 26th January 1959

BRADFORD JUNIOR BRANCH. *Recent Developments in the use of Terylene Staple Fibre in the Woollen and Worsted Industry.* P. W. Eggleston, Esq. (Imperial Chemical Industries Ltd.). Institute of Technology, **Bradford** 7.15 p.m.

Saturday, 31st January 1959

MANCHESTER SECTION. Annual Dinner and Dance, Grand Hotel, **Manchester.** 6 p.m. for 6.30 p.m.

Tuesday, 3rd February 1959

LEEDS JUNIOR BRANCH. *Colour Matching.* E. Bellhouse, Esq., B.Sc. Lecture Theatre, Department of Colour Chemistry and Dyeing, The University, **Leeds.** 3.15 p.m.

Thursday, 5th February 1959

MIDLANDS SECTION. *Developments in Modern Dry-cleaning Techniques.* E. J. Davies, Esq., M.Sc. Gas Board Theatre, **Nottingham.** 7 p.m.

Friday, 6th February 1959

LONDON SECTION. *Colour Photography.* Dr. R. W. G. Hunt (Kodak Ltd.). The Royal Society, Burlington House, **London W.1.** 6 p.m.

Tuesday, 10th February 1959

BRADFORD JUNIOR BRANCH. *New Levelling Agents in Acid and Direct Dyebaths.* G. H. Lister, Esq., B.Sc., Ph.D. (Sandoz Products Ltd.). Institute of Technology, **Bradford.** 7.15 p.m.

NORTHERN IRELAND SECTION. *Emulsion Thickenings—Possibilities in Textile Printing.* T. L. Dawson, Esq., B.Sc., Ph.D., A.R.I.C. (Imperial Chemical Industries Ltd.). Grosvenor Rooms, **Belfast.** 7.30 p.m.

SCOTTISH SECTION. *The Use of Antistatic Agents in Textile Processing.* A. E. Henshall, Esq., B.Sc. (Imperial Chemical Industries Ltd.). (Joint meeting with the Textile Institute.) St. Enoch Hotel, **Glasgow.** 7.15 p.m.

Thursday, 12th February 1959

WEST RIDING SECTION. *New Ideas in the Application of Phthalocyanine Derivatives to Textiles.* Dr. F. Gund. (Farbenfabriken Bayer). Griffin Hotel, Boar Lane, **Leeds.** 7.30 p.m.

Tuesday, 17th February 1959

HUDDERSFIELD SECTION. *The Use of Antistatic Agents in Textile Processing—Advantages and Disadvantages.* A. E. Henshall, Esq., B.Sc. (Imperial Chemical Industries Ltd.) Silvios Cafe, **Huddersfield.** 7.30 p.m.

Thursday, 19th February 1959

MANCHESTER JUNIOR BRANCH. *Chlorite Bleaching.* W. J. Watts, Esq., B.Sc. Room J/B 16 — Chemical Engineering Building (Jackson Street), College of Science and Technology, **Manchester.** 4.30 p.m.

SCOTTISH JUNIOR BRANCH. *Colour Vision.* Dr. Mary Collins (Department of Psychology, Edinburgh University), also *How the World Looks to a Colour Defective* (a short colour film obtained through the courtesy of the Department of Naval Research, United States of America). Technical College, **Paisley.** 7.30 p.m.

Friday, 20th February 1959

MANCHESTER SECTION. *Emulsion Thickenings. Possibilities in Textile Printing.* T. L. Dawson, Esq., B.Sc., Ph.D., A.R.I.C., F.C.S. (Imperial Chemical Industries Ltd.). The Textile Institute, 10 Blackfriars Street, **Manchester.** 7 p.m.

Wednesday, 25th February 1959

BRADFORD JUNIOR BRANCH. *Vat Dyeing of Cotton Piece Goods by Pre-pigmentation Routes.* M. R. Fox, Esq., F.T.I., F.S.D.C. and J. F. Mawson, Esq., B.Sc. (Imperial Chemical Industries Ltd.). Institute of Technology, **Bradford.** 7.15 p.m.

continued on page xli

THE JOURNAL
OF THE
Society of Dyers and Colourists

Volume 74 Number 12 DECEMBER 1958 *Issued Monthly*

Proceedings of the Society

THE FOURTEENTH JOHN MERCER LECTURE

The Influence of Fibre Types on Dyeing Methods

J. S. Ward

Meeting held at the Grand Hotel, Leicester, on 3rd May 1957, Mr. Clifford Paine (President of the Society) in the chair

An account is given of the many factors which influence the dyeing method adopted for a particular fibrous material. Some of these factors, such as the diffusion rate and the affinity of dyes, are fundamental; others, such as the colours required or variability in dyeing properties, are accidental; whilst many, such as the volume of business or the cost of dyes, are dependent upon the economic structure of the industry. All must be accommodated in a successful dyeing process.

We in the Dyeing and Finishing Industry exist primarily to provide a service to the Textile Industry at large. The outstanding feature of the present age in textiles is the ever growing number of new raw materials and manufactures. These new products inevitably and quite quickly find their way into our dyehouses, and we are required, often at short notice, to provide satisfactory methods for dyeing and finishing them. Invariably we submit the new materials to existing processes, but rarely do we meet with complete success. This is not surprising in view of the complex requirements of a successful dyeing process, which are—

(i) The materials must be dyed to the desired colour, with sufficient uniformity and sufficient permanence to satisfy the customer or consumer in the use for which they are intended.

(ii) The characteristic properties of the materials must be conserved, unless it is agreed with the customer to modify them in a prescribed manner.

(iii) The cost of doing the work must bear a satisfactory relation to the price obtainable.

The simultaneous observation of these conditions, even with the older manufactures, may be quite a difficult matter, and we are often obliged to compromise. A very broad compromise may be satisfactory, particularly in the early stages of development of a new product in order to permit overall progress to be made, but in face of competition or more stringent requirements we are often obliged to reconsider our existing methods and see what we can do to improve them. Quite often the development of new or considerably modified methods is found to be necessary.

The research and technical service departments of dye makers, fibre makers, and machinery makers are often able to contribute to these developments by carrying out investigations on behalf of the industry, and have built up over the years a considerable body of information on the behaviour of dyes, fibres, and dyeing machines during the dyeing process, much of which has been published. This information, allied to that contributed by university departments, technical colleges, research institutes, and, of course, dyers themselves, allows a better understanding of the mechanisms of our dyeing processes; our appreciation of the principles involved in these processes has improved considerably in recent years. It is now clear that certain common principles apply to dyeing processes in general, and others to particular types of dyeing process. In order to make use of these principles in the development of a new method, or the solution of a practical problem, it is usually necessary to have actual data on the properties of the fibres, dyes, or machines concerned. It is the purpose of this lecture to summarise this background work, particularly that portion relating to the properties and consequent behaviour of different types of fibre in relation to both established and proposed methods of dyeing.

Transfer of Dye to Fibre

The first objective of dyeing processes is to colour the materials to the desired shade with adequate fastness and uniformity. In order to do this we must first find suitable dyes and then transfer

them uniformly to the assembly of fibres in the right amount. To some extent we can consider this part of the process in isolation. It is controlled by three principal factors.

1. DIFFUSION

The basic requirement is that the dye should be capable of diffusion into the fibre from its surroundings. The technical consequence of depositing dye on the outer surface of the fibre, rather than within, is poor fastness to rubbing and possibly to other agencies. There is one exception to this, in the case of resin-bonded pigments. The application of this method in dyeing is not yet fully developed, except for pastel colours, but it is widely used in printing. In this case the basic requirement is modified to allow the extension of the substrate in the form of binder to envelop the colouring matter without diffusion taking place.

Fibres vary widely in the rate of diffusion of dyes into them from aqueous dyebaths. At a given temperature, the rate depends upon the relative sizes of the dye molecules (or particles) and the channels in the fibre through which they must pass. The larger the dye and the smaller the channels in the fibre, the more difficult it is for dye to diffuse into the fibre. Diffusion rates are influenced greatly by temperature—the higher the temperature, the higher the rate. The sizes of dye molecules in solution vary approximately in the order—

> Disperse dyes < Levelling acid dyes < Indigoid leuco-vat dyes = Basic dyes < Anthraquinone leuco-vat dyes = Aggregated acid dyes < Metal-complex dyes < Direct dyes.

Dry fibres all have relatively compact structures; on wetting, the structure opens to an extent depending upon fibre type. The sizes of the channels which are formed vary in the order—

> Terylene < Tricel < Orlon < Dicel < Nylon < Perlon = Wool < Viscose rayon < Cotton < Fibrolane.

Nearly all known dyes diffuse into cotton, viscose rayon, or Fibrolane at 100°c. Only the smallest disperse dyes, diffuse into Terylene at this temperature. The other fibres exhibit intermediate behaviour; Table I shows the temperature required for diffusion to proceed at a useful rate for various combinations of dye and fibre. Thus disperse dyes, which diffuse readily into Dicel at low temperatures, require increasingly higher temperatures for Orlon, Tricel, and Terylene to achieve a similar rate of diffusion (see also Fig. 1). Many anthraquinone vat dyes, which will diffuse into cotton or viscose rayon at room temperature, require a high temperature to diffuse into nylon, and do not enter Tricel at all.

Advantage has been taken recently of the very high rate of diffusion of the levelling type of acid dye into cellulose fibres such as cotton and viscose rayon, in the establishment of a new range of dyes for these fibres, the reactive dyes, which are based on the acid dyes. The novelty of these dyes is the reaction which takes place under the influence of alkali between the dye and fibre, linking the two together, but also important from the practical point of view is that the diffusion of dye into the fibre, which takes place before the reaction step, can take place at low temperatures in a very short time.

If it is particularly desired that a certain dye or type of dye with a normally low rate of diffusion be used, steps can be taken to increase this rate by three methods—

(a) *Increase in Temperature*

The normal maximum temperature of dyeing possible in ordinary dyeing equipment is that of boiling water, but by using completely enclosed dyeing equipment higher temperatures may be used, as in the case of Terylene, for which temperatures up to 130°c. are employed. In this case, by going from 100° to 120°c. the diffusion rate of disperse dyes is increased by a factor of 10–20[1]. The restrictive maximum temperature of 100°c. occasioned by the use of water as dye solvent can be avoided by using a different solvent boiling at a higher temperature. Several processes of this type have been suggested, one of the most original being the use of molten urea. The fabric is impregnated with a dispersion of dye in a strong solution of urea, the water removed by drying, and the whole then heated sufficiently to melt the urea at a temperature of 140°c. Molten urea is an excellent dye solvent, the liquor ratio is very low, and the temperature is very high; under these conditions transfer of dye to the fibre surface and diffusion of dye into the fibre can both take place rapidly[2].

In normal dyeing processes water, in addition to causing swelling of most fibres, acts as dye solvent and transfer agent, both outside and inside the

TABLE I

Approximate Temperatures (°C.) necessary for Adequate Diffusion

Dyes ... / Fibre	Disperse	Levelling Acid	Indigoid Leuco Vat and Basic	Anthraquinone Leuco Vat and Aggregated Acid	Direct Class A	Direct Class B
Terylene	110	—	—	—	—	—
Tricel	90	110	—	—	—	—
Orlon 42	80	95	100	—	—	—
Dicel	60	80	90	—	—	—
Nylon	50	70	80	95	100	—
Perlon L	40	60	70	90	95	100
Wool	40	60	60	85	95	100
Viscose rayon	20	30	30	40	50	70
Cotton	20	20	20	40	50	70
Fibrolane	20	20	20	40	50	70

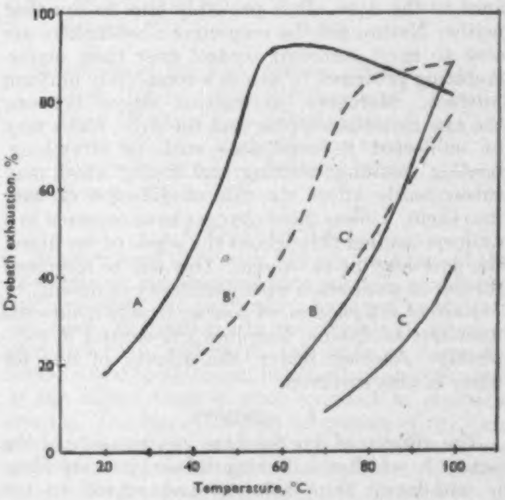
fibres. As a solvent, its purpose is to break down the larger particles of dye into smaller particles, ultimately of molecular dimensions. In the case of disperse dyes, this breakdown can be accomplished in another way— by sublimation— which does not require water to be present. Furthermore, the available evidence suggests that water does not penetrate Terylene to any great extent, and that little increase in the size of the channels within the fibre occurs in the presence of water. Hence water is not strictly necessary to the dyeing of Terylene with disperse dyes. Various methods which take advantage of this have been suggested, notably the Thermosol process and the process suggested by the British Rayon Research Association using the fluidised bed. In both these methods the fabric is impregnated with a dispersion of a disperse dye and dried; then the whole is heated to a high temperature for a short time, the conditions being suitable for both sublimation of dye and rapid diffusion into the fibre.

(*b*) *Increase in the Size of the Channels in the Fibre*

By using a liquid other than water, the opening of the fibre structure may in some cases be increased. This method has often been used to allow vat dyes or acid dyes, which are of too great a molecular size to diffuse into the normally water-swollen fibre, to be used on cellulose acetate. The use of 70:30 alcohol–water solutions to apply vat dyes to the acetate portion of cellulose acetate–cotton furnishing fabrics has an interesting effect [3]. The swelling of the acetate is increased to such an extent that the acetate accommodates 60–70% on its weight of the mixed solvent, compared with 20–25% of water alone; whilst the cotton swells only 10–15% instead of the normal 40–50%. As a result the vat dyes diffuse rapidly into the cellulose acetate but very slowly into the cotton, a complete reversal of the normal effect.

(*c*) *Exchange of the Liquid within the Fibre for Another Liquid in which the Dyes are more soluble*

This is the basis of the "carrier" method, although in practice the action of "carriers" is probably a combination of (*b*) and (*c*). The amount of carrier required is only small, since it is normally insoluble or only sparingly soluble in water and is largely transferred from a dispersion in the dyebath to the fibre, either before dyeing or in the early stages of the dyeing process. The carrier method is applicable particularly to disperse dyes owing to their normally low solubility in water. Satisfactory carriers are to a large extent specific to particular fibres. Thus diphenyl, which is a moderately good carrier for disperse dyes on Terylene, is much less satisfactory on Tricel and has no effect at all on the rate of diffusion of dyes into Orlon. On the other hand, esters such as dimethyl phthalate are most effective on Tricel. No really effective carrier for acrylic fibres has yet been found. The comparative effects of carrier dyeing and high-temperature dyeing on these fibres are shown in Fig. 1 and Table II.



A Dicel (secondary cellulose acetate)
B Tricel (cellulose triacetate)
C Terylene (polyester)
B' Tricel + carrier (dimethyl phthalate)
C' Terylene + carrier (diphenyl)

FIG. 1— Typical Temperature-range Properties of a Disperse Dye on Various Fibres (liquor ratio 40:1; time of dyeing 2 hr.)

TABLE II

Comparative Absorption (%) of Disperse Dyes by Tricel, Orlon 42, and Terylene under Various Conditions of Dyeing

(50:1 liquor ratio for 2 hr.)

Dye	*Colour Index* No.	Fibre	Dyeing Conditions Carrier None, Temp. 95°c.	Carrier *p*-Phenylphenol, Temp. 95°c.	Carrier None, Temp. 120°c.
4% Serilene Dark Blue G	C.I. Disperse Blue 35	Tricel	75	81	80
		Orlon 42	20	40	51
		Terylene	20	85	86
5% Duranol Blue GNS	C.I. Disperse Blue 26	Tricel	59	70	73
		Orlon 42	15	31	40
		Terylene	24	67	79
3% Serisol Fast Scarlet BD	C.I. Disperse Red 1	Tricel	96	96	98
		Orlon 42	18	28	47
		Terylene	22	83	93
3% Duranol Blue 2G 300	C.I Disperse Blue 24	Tricel	80	96	93
		Orlon 42	12	30	42
		Terylene	12	85	93

The recently introduced Vapocol (ICI) process[4], in which secondary acetate or triacetate fabrics are padded in disperse dye, dried, and then exposed to the vapour of boiling trichloroethylene, is a combination of methods (*b*) and (*c*). The trichloroethylene condenses on the fibre, and acts as a swelling liquid to provide large dye channels containing a good dye solvent at a relatively high temperature (88°c.). Diffusion rate is therefore high. If the method is to be used on Terylene, ethylene dichloride must be substituted for trichloroethylene in order to produce the requisite swelling effect.

In this discussion we have assumed that all samples of a given fibre type exhibit approximately the same behaviour with respect to diffusion of dyes. This is in fact correct, but the extent of the approximation is of extreme importance to the dyer. It is probably true to say that neither Nature nor the respective fibre-makers are able to exert sufficient control over their manufacturing processes to ensure a completely uniform product. Moreover, at various stages between the raw-material supplier and the dyer, fibres may be subjected to conditions such as stretching, heating, steaming, wetting, and drying, which may subsequently affect the rate of diffusion of dyes into them. Unless these changes have occurred in a uniform manner throughout the whole of the fibres, the dyer may be in trouble. This will be discussed further in connection with uniformity of dyeing.

Rate of diffusion is, of course, closely connected with rate of dyeing, but does not control it completely. Another factor, the affinity of dye for fibre, is also involved.

2. AFFINITY

The affinity of dye for fibre is a measure of the extent to which dye, having diffused into the fibre, is withdrawn from solution and affixed to the internal surface of the fibre. The cause of this withdrawal is a specific attraction between the dissolved dye and the fibre. The attraction between certain ionised (electrically charged) groups occurring in fibres and dye ions carrying the opposite charge is particularly specific. (There is also a repulsion between charged groups and dye ions of similar charge.) Thus under particular conditions of acidity or alkalinity, which are necessary to cause ionisation of the appropriate groups in the fibre, the positively charged basic groups in wool or nylon attract the coloured anions of acid dyes; similarly, the negatively charged acidic groups in silk or Orlon attract the coloured cations of basic dyes.

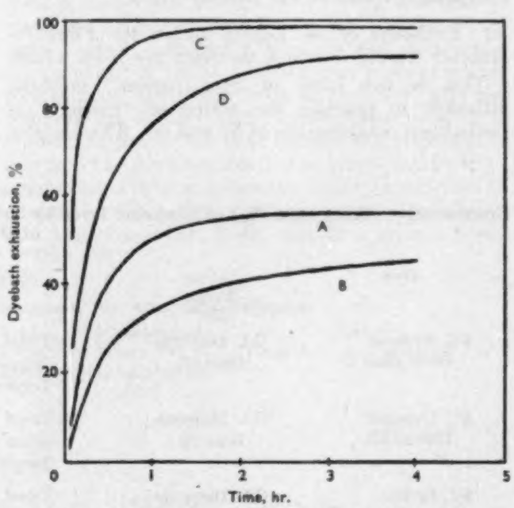
There is in addition a less specific attraction between all dyes and fibres, the magnitude of which in any particular case appears to depend upon the solubility of the dye, the size and shape of the dye molecule, and the chemical composition of the fibre. This type of attraction augments the more specific attraction mentioned above.

With a particular combination of dye and fibre, affinity may vary considerably according to the dyebath conditions employed. With a particular dye and fixed conditions, it may vary considerably according to the fibre being dyed. Affinity is reduced with increase in temperature, whatever the dye and fibre.

The affinity of a dye for a fibre under a particular set of dyeing conditions determines the equlibrium exhaustion of the dyebath and also plays a large part in determining the rate of dyeing. When affinity is high, the major portion of the dye entering the fibre is attracted to the internal surface before it has diffused very far. Diffusion rate need not therefore be high to obtain a high rate of dyeing. A similarly high rate of dyeing may be obtained in another case in which affinity is low and diffusion rate high, but here penetration of dye into the fibre would be considerably greater than in the first case.

Dyers in general are liable to judge all cases of poor dyeability as being due to lack of affinity. This is seldom the case: more often the difficulty is due to low rate of diffusion. A particular example is the behaviour of Terylene towards disperse dyes: a low rate of uptake of these dyes is wholly due to a low rate of diffusion, the affinity of these dyes for Terylene being of the same order as for secondary cellulose acetate. A genuine instance of low affinity, however, is that of disperse dyes with acrylic fibres. It is possible to produce acrylic fibres of the Orlon type with quite open structures in which disperse dyes diffuse readily, but with these fibres, as with Orlon, equilibrium exhaustions of disperse dyes are quite low, even with pale colours. This appears to be due to lack of the more general attraction between dye and fibre which I have just described.

Introduction of a more specific ionic attraction into the system increases the affinity of dyes enormously (Fig. 2). This is shown by the behaviour of the basic dyes, which whilst diffusing more slowly than many disperse dyes, give much higher dyebath exhaustions at equilibrium. Similar



A, B Disperse dyes (no ionic attraction)
C, D Basic dyes (dye ion positively charged, fibre sites negatively charged) or acid dyes by cuprous ion method (dye ion negatively charged, fibre sites positively charged)

FIG. 2— Typical Behaviour of Dyes on an Acrylic Fibre (liquor ratio 40 : 1; temperature 100°C.)

TABLE III

Comparative Properties of Different Dyeing Systems

Affinity	Diffusion Rate	Dyeing System Fibre	Dye Class	Conditions
High	Low	Terylene	Disperse	95°c.
		Viscose rayon	Direct (Class B)	95°c. 10% NaCl
Low	High	X.51 Acrylic	Disperse	95°c.
		Viscose rayon	Direct (Class A)	95°c. 10% NaCl
		Cotton	Azoic coupling components	40°c.
		Cotton	Procion	40°c.
High	High	Viscose rayon	Anthraquinone leuco vat	60°c.
		Viscose rayon	Direct (Class C)	95°c. 10% NaCl
		Secondary cellulose acetate	Disperse	80°c.
Low	Low	Orlon	Disperse	90°c.

behaviour is shown by acid dyes applied to acrylic fibres by the cuprous ion dyeing method. This method is an example of high affinity being induced in a dyeing system by the formation within the fibre of ionised (positively charged) groups to which acid may be attached. The Katanol and tannic acid–antimony mordants for basic dyes on cotton act in a similar way, but with reversal of electrical charges on the dyes and groups attached to the fibre.

Instead of using the cuprous ion method of applying acid dyes to acrylic fibres, it is possible to arrange that the appropriate basic groups are incorporated during fibre manufacture. Such a fibre is Acrilan: this acrylic fibre contains weakly basic groups requiring strongly acid dyebath conditions to allow full ionisation, but under such conditions the affinity for acid dyes is high. This high affinity is very largely due to the ionic interaction, as in the case of the cuprous ion method; the more general attraction between dye and fibre contributes little. The high affinity of aggregated acid dyes for wool, which allows them to be applied from a neutral dyebath, has been attributed to this general attraction. The fact of the general attraction being low in the case of Acrilan means that all types of acid dye have similar affinities and require similar strongly acid conditions.

Many azoic coupling components, in the normal alkaline solution, have quite low affinities for cotton and viscose rayon, but high diffusion rates, and are commonly applied to cotton yarn or fabric by a simple impregnation process. In the case of cotton yarn this is followed by a heavy squeezing or wringing to remove excess liquor. The impregnation–wringing process cannot be used with viscose rayon continuous-filament yarn owing to the likelihood of mechanical damage, but those coupling components with the highest affinity can be successfully applied by a normal dyeing process at low temperature, advantage being taken of the high diffusion rate and the increase in affinity with fall in temperature to obtain adequate penetration of the fibre and reasonable dyebath exhaustion.

Examples of the four extreme cases—

High affinity – High diffusion rate
High affinity – Low diffusion rate
Low affinity – High diffusion rate
Low affinity – Low diffusion rate

are given in Table III.

3. SATURATION

Saturation of fibre with dye occurs when all the positions on the internal fibre surface, which can accommodate a particular type of dye, are occupied. Saturation can occur with all types of dye and fibre, but in the majority of cases the amount of dye which can be absorbed at saturation is far higher than is ever required in practical dyeing. The cases in which saturation of the fibre has a bearing on practical dyeing problems are principally those in which the dyes are attracted to specific groups in the fibre, and the number of these groups is small. When the electrical charges of these groups are fully neutralised by adsorption of dye, further absorption can take place only through the more general attraction of dye and fibre surface. In the case of nylon, which, compared with other acid-dyeing fibres such as silk and wool, contains only a low concentration of basic groups, the affinity of levelling acid dyes is due principally to the ionic attraction, whereas that of the 2:1 metal-complex neutral-dyeing acid dyes depends to a much greater extent on the attraction of large molecule for fibre surface. Thus the levelling acid dyes exhibit a well defined maximum absorption, depending upon the number of basic groups in the fibre, whilst the 2:1 metal-complex dyes exhibit no such maximum.

The poor build-up of certain disperse dyes on secondary cellulose acetate and Orlon has also been attributed to saturation of the fibre; the saturation level of disperse dyes appears to differ considerably from dye to dye and, with the same disperse dye, from fibre to fibre (Table IV).

Cost of Dyeing

The cost of a particular dyeing process is made up in the first place of the cost of the dyes and other materials required and of the cost of the

TABLE IV

Saturation Absorptions of Disperse Dyes (%)

Disperse Dye	*Colour Index* No.	Secondary Cellulose Acetate[5] 85°C.	Nylon[8] 85°C.	Orlon 42[8] 95°C.	Terylene[6] 100°C.
Dispersol Fast Yellow G 300	C.I. Disperse Yellow 3	—	—	1·4	—
Dispersol Fast Yellow A 300	C.I. Disperse Yellow 1	16·0	5·0	3·0	4·6
Dispersol Fast Orange G 300	C.I. Disperse Orange 3	5·1	2·0	1·1	4·8
Duranol Red 2B 300	C.I. Disperse Red 15	11·2	4·4	1·8	10·7
Duranol Violet 2R 300	C.I. Disperse Violet 1	8·3	4·9	—	4·7
Duranol Brilliant Blue CB 300	C.I. Disperse Blue 1	—	—	3·5	—
Duranol Blue Green B 300	C.I. Disperse Blue 7	—	—	1·0	—

dyeing process itself. The latter includes the length of time during which the dyeing machine is occupied, the amount of supervision required, and a proportion of the return on capital employed in the process. In the second place it is made up of the cost of material spoiled during the dyeing process, and of reprocessing faulty material. The cost of dyes when dyeing pale colours is generally quite small, but when dyeing deep colours it may be considerable and represent a high proportion of the total cost of dyeing. In this respect it is clearly to the advantage of the dyer that his dyes should have high affinity, so as to secure full utilisation of the dyes which are present in the dyebath.

The wastage of dye which can occur is well illustrated by an attempt to match heavy worsted suiting colours on an acrylic fibre with disperse dyes. Little more than 50% of the dye present can be transferred to the fibre even if the dyeing is carried to equilibrium. In contrast to this is the behaviour of basic dyes on the same fibre: except with extremely heavy depths, the exhaust dyebath is almost water-white, in spite of the low rate of diffusion of these dyes. Good dyebath exhaustion due to high affinity is advantageous also from the point of view of matching and reproducibility of dyeings, for once a recipe has been established, the dyer need only take care with his weights of material and dye for close repeats to be obtained on each subsequent occasion. This is well known to the wool dyer. Ease of matching contributes to the reduction of dyeing time. The other contributory factor is the actual time required to build up the colour uniformly. With dyeing systems having normally slow diffusion rates we can speed up the process by the methods already discussed, but each of these must entail some cost additional to that of a normal process— the use of organic solvents or carriers or the installation of new equipment. The choice of method will depend upon volume of business and the type of work being done. Many slubbing and yarn dyers have installed high-temperature dyeing machines for the dyeing of Terylene, in which heavy depths can be obtained in reasonable dyeing times, but piece dyers generally have been slower in adopting this technique owing to the high cost of suitable equipment and the greater manipulative difficulties.

There are large differences in the cost of dyes themselves. In general, we pay for complexity of dye, novelty of dye, and fastness of dye. Of the two main groups, azo dyes are generally cheaper than anthraquinone dyes. Thus we can say that the yellow, orange, and red dyes are cheaper than the blue and green dyes. This is particularly true of the simpler dyes, such as disperse dyes and levelling acid dyes, and is true also in a comparison of the azoic dyes with the vat dyes. A comparison of the cost of dye for the various fibres can be made only on the basis of equivalent fastness: for a given fastness, those fibres can be dyed most cheaply, so far as dye cost is concerned, which can be dyed with small dyes, with azo dyes, and with the older dyes. In this respect, the acid-dyeing fibres have a distinct advantage. For all normal apparel purposes, wool can be dyed more cheaply than any other fibre: the two principal ranges of dyes, the aggregated acid dyes and the chrome dyes, are composed largely of the groups just mentioned. "Disperse-dyeing" fibres are at a disadvantage compared with wool because of the relatively expensive anthraquinone blues, which are required for practically all deep colours. "Direct-dyeing" fibres are at a disadvantage because of the greater complexity of dyes and after-treatments required to give them sufficient wet fastness, but when sulphur dyes can be used, the price and the fastness compare well with those of chrome dyes. Nylon in staple form can also be dyed as cheaply as wool with acid dyes, but the regenerated protein fibres, like the cellulosic fibres, have a relatively open structure, so that more complex dyes must be used to give fastness equivalent to that of wool dyed with acid dyes.

Whilst considering the subject of fastness and cost of dye, we must not forget the special contribution which man-made fibres have made in the method of coloration known variously as "mass-pigmentation", "spin-dyeing", etc. This has been standard practice with secondary cellulose acetate yarns and viscose rayon yarns and staples for many years now, and as new fibres appear, it is seldom long before we see at least a small range of coloured fibres prepared by this means. With viscose rayon the method offers equivalent wet-fastness and often equivalent or better light-fastness to the best vat and azoic dyes at appreciably lower cost, and with cellulose acetate a range of colours and fastnesses many of which could not be achieved at all by other means.

Uniformity of Dyeing

One of the greatest headaches of the dyer is to obtain sufficient uniformity of dyeing. The

standard of regularity demanded differs considerably from one form of material to another, being least with loose stock and slubbing dyeing and greatest with the dyeing of continuous-filament yarns or fabrics. Whatever the type of material being dyed, however, the problem of unlevel dyeing usually crops up.

There are two main types of unlevelness. The first, which is entirely due to defection on the dyer's part, is caused by subjecting different parts of his material to different conditions of dyeing. The second, which is not due to any fault on the part of the dyer, but which he is invariably called upon to correct, is due to irregular dyeing behaviour of the material itself, such that, although the dyer may subject the whole of it to precisely the same conditions of dyeing, an unlevel result may be obtained.

The first type of uneven dyeing may be avoided by due care and attention on the part of the dyer and may often be corrected even when it has occurred. The second type can seldom be avoided, even though the dyer may know that his material will behave irregularly, but may in many cases be corrected. Poor penetration of yarns and fabrics, listing and ending of jig-dyed materials, and rope-marking and streakiness of winch-dyed materials are examples of the first category; whilst warp stripiness and weft bars and skitteriness are often caused by irregularly dyeing yarns and fibres.

In order to avoid the first type of unlevel dyeing, the dyer must ensure that the relative movement of dye liquor and material is high enough, that the folds of rope-dyed material are changed often enough, and that the rate of dyeing is slow enough to allow each portion of the material to come into contact with dye liquor of a particular concentration at a particular temperature for the same length of time during the whole of the dyeing period. Machines such as winch-dyeing machines and yarn-dyeing machines with liquor flow have been designed to move either liquor or goods relative to the other component at a suitable rate by mechanical means. The jig-dyeing machine, which operates on a different principle, moves goods relative to liquor rather less frequently, and uniformity depends upon both the rapid impregnation stage and the longer dyeing stage. The extent of the mechanical movement of liquor or goods is determined in any given case by the material being dyed and the machine in use, and can seldom be altered to meet particular circumstances. The main control which the dyer exerts is on the rate of dyeing. Several types of control are possible according to the dyeing system in use. Assuming for the moment that unlevelness of this type has arisen, it can be cured by transfer of dye from an overdyed to an underdyed portion of the material, so that the whole of the material is in equilibrium with the dyebath. This can be obtained in a reasonable extension of dyeing time only when the dye has a sufficiently high rate of diffusion under the conditions of temperature, etc. obtaining. The number of dyeing systems in which it is possible to obtain a sufficiently high rate of diffusion to overcome gross unlevelness is small. At temperatures up to the boil we can expect to do so only with—

- Levelling acid dyes on wool and regenerated protein fibres
- Class A direct dyes on cellulosic fibres
- Weak-alkali type anthraquinone vat dyes on cellulosic fibres
- The most rapidly diffusing disperse dyes on secondary cellulose acetate and nylon.

In all other cases diffusion rates (up to 100°C.) are low, and the dyer must not let this unlevelness occur, which means that dyeing rate must be controlled at a sufficiently low level. We have seen that the rate of dyeing is made up of two factors—diffusion rate and affinity. Either or both of these can be used to control rate of dyeing. The ideal way is to operate with maximum diffusion rate throughout the whole of the dyeing period, and control affinity from low in the early stages to high towards the end of dyeing, so that we obtain the maximum possible migration whilst dyeing is proceeding, and eventually obtain good exhaustion of the dyebath. We can control affinity in the case of the acid-dyeing fibres— wool, nylon, silk, and Acrilan— by controlling the acidity of the dyebath; similarly, but in the opposite sense, with the basic-dyeing acrylic fibres. In the case of cellulosic fibres affinity may be controlled with many dyes by controlling the salt content of the dyebath. For other dyes the salt content may be initially too high to allow control because of adventitious salt from water or dye powder itself, as in the case of many Class C direct dyes, or because of the unavoidable addition of alkali and reducing agent in the case of vat dyes. These Class C direct dyes and strong-alkali vat dyes are in many ways similar in behaviour to disperse dyes. We know of only one method by which the affinity of such dyes may be controlled so as to start with low affinity and gradually increase it during the dyeing process. This is to commence dyeing at a high temperature, which is gradually lowered during the dyeing process. If we start with low affinity obtained by large additions of dispersing or restraining agent, we must end with low affinity and hence poor exhaustion of the dyebath. In those cases in which affinity cannot be satisfactorily controlled, we must control rate of dyeing by diffusion rate only, i.e. by control of temperature, which is a less satisfactory method overall. It is possible, however, in many cases by close temperature control of diffusion rate to secure even absorption of dye and avoid unlevelness.

1. COVERING OF IRREGULAR MATERIAL

I have already discussed the difficulties of providing a completely uniform fibre. The differences which may arise in the dyeing behaviour of raw fibrous material are more obvious in the case of continuous-filament yarns than with staple, since in the latter case blending of many different batches is usually practised by the spinner, and the variation is to a large extent covered. Differences which occur owing to irregular heating, wetting, etc. of staple yarns after spinning will, however, show in the same way as in continuous-filament yarns. Differential dyeing behaviour is sometimes due to differences in affinity or saturation value in

different batches. The classic example of the latter is the differential dyeing of nylon with variation in basic end-group content. More often, however, differential dyeing is due to variation in rate of dyeing, the equilibrium exhaustions for the various fibres being very similar. Variations of the first type can seldom be covered up completely by the dyer except by changing the type of dye; the majority of nylon continuous-filament material is, of course, dyed with disperse dyes for this very reason, since variations in end-group content do not affect the absorption of these dyes. The second and principal type of differential dyeing can always be covered by dyeing until all fibres are in equilibrium with the dyebath. The problem is really identical with that of correcting an unlevel dyeing, and the same conditions apply: a high rate of diffusion is essential, and unless this can be obtained by the means already discussed, the faults will persist.

2. PADDING METHODS

The foregoing discussion relates entirely to dyeing methods in which dye is exhausted from the dyebath slowly over a period of time. In the other type of dyeing method the material is impregnated usually by a padding operation, and the dye fixed at a subsequent stage. Such methods initially came into prominence for the application of colouring matters in which the components had very high diffusion rates and low affinity and were subsequently converted within the fibre to the final colouring matter. The processes for applying Aniline Black, Mineral Khaki, Para Red, etc., principally to cotton piece goods, were the first continuous dyeing methods. The use of an impregnation or padding process does not necessarily imply continuous dyeing but does imply lack of dependence on affinity of dye. In fact, when affinity is sufficiently high to give a high rate of dyeing at low temperature, special methods must be adopted when padding to prevent, or allow for, the change in concentration of the padding solution caused by absorption of dye by the fibre in passing through it [7].

Special advantages of padding methods are the uniformity of dyeing and low liquor ratio which are obtainable by their use. The dye is placed in position mechanically, and if the impregnation is uniform, we have a simple method of overcoming many of the difficulties of exhaustion techniques. Most impregnation processes use conventional padding methods, in which two of the main difficulties are to maintain constant pressure across the whole width of the rolls and to squeeze light-weight continuous-filament fabrics satisfactorily, particularly those containing hydrophobic fibres. Recent developments in the design of pad-mangles have been directed to overcoming the first problem; the second is due to the smaller number of suitable capillary spaces between the individual fibres compared with a staple-fibre fabric. The volume of liquor passing through the nip with the fabric must be immediately blotted up by these capillary spaces, otherwise the dye liquor runs freely on the surface of the fabric and unlevel results are obtained. This can be avoided to a large extent by increasing the viscosity of the padding liquor by the incorporation of a thickener. Solid thickeners must, however, be capable of being removed in a subsequent operation. Recent developments in the use of oil-in-water emulsions point the way to overcoming this disadvantage. Emulsions of this type appear to show a particular advantage in the dyeing of nylon continuous-filament fabrics with the metal-complex acid dyes: application of these dyes by conventional methods would show up the inherent irregularity of the nylon yarns. The use of oil-in-water emulsions enables a high-viscosity dye liquor to be used for padding and the affinity to be kept low during this operation: the dye is held in the oil phase, and thus kept separate from the acid-fixing agent, which is held in the water phase. When the emulsion is subsequently broken by steaming, viscosity is reduced, affinity and diffusion rate are increased, and a uniformly dyed product with good colour fastness is obtainable.

The development of pad–dyeing methods and its obvious extension to continuous dyeing has taken place almost entirely with materials made of cotton. There are several reasons for this. Firstly, the dyes which are used for cotton, particularly for the fast dyeings, are particularly suited to application on the pad: for example, solubilised vat dyes and azoic coupling components are most economically applied in this way, since they have low affinity; the leuco vat dyes and sulphur dyes are more uniformly applied in this way, via the pigment (or unreduced) low-affinity form. Secondly, well prepared cotton fabrics are in general sufficiently absorbent to have the blotting action necessary to successful padding. Thirdly, the amounts of cotton fabrics required to be dyed with these types of dye are sufficient to justify capital expenditure on continuous-dyeing ranges.

Of the many aspects of pad–dyeing, just two may be mentioned. The first is the use of vat dyes in the unreduced form. These pigment powders and pastes are the basis of most attempts to secure greater uniformity of dyeing with the vat dyes (except in pastel colours, when the water-soluble leuco esters can be used), since they have practically no affinity for the fibres and the specially prepared types form good dispersions. They allow uniform impregnation of both fabrics and yarn packages and are readily converted to the reduced form, which is rapidly absorbed by the fibre by reason of high affinity and high diffusion rate. The second is the Standfast molten-metal process, which permits uniform impregnation and fixation in one stage, the latter because of the very small volume of the padding trough, and the virtual absence of air in the system, which allow reduced vat dyes to be padded successfully. Because of the short passage through the molten metal, the process cannot be used for other dyeing systems with a slow rate of dyeing.

Behaviour of Fibres during Dyeing

So far, we have considered only those factors which relate to the actual absorption of dye by the fibre. We must now examine the other main

aspect of dyeing— the handling and behaviour of the materials whilst dye absorption is proceeding. The first part of our investigation has shown us that, in order that dye absorption shall proceed satisfactorily and that the dyed material shall have the desired fastness, we must subject our fibrous materials to three main influences—

(i) Water or other swelling agents, which we need to dissolve and transport the dye and swell the fibre

(ii) High temperatures, which we need to assist the diffusion processes

(iii) Various chemical reagents, which we need to solubilise or modify the dyes, or to activate the receptive positions in the fibre.

Under these influences we must continually change the relative positions of dye liquor and goods by circulation of liquor or movement of goods so as to submit each portion of the material, so far as possible, to the same conditions of dyeing. The materials may thus be subjected to mechanical forces of various types— pressure, tension, torsion, bending, and so on.

But it is a condition of our dyeing processes and indeed of our remaining in business that we should conserve or in certain cases specifically modify the characteristic properties of the materials we are processing. The greater our understanding of the influences at work, the more likely are we to be able to control these properties.

Unfortunately, this aspect of dyeing has not yet been fully investigated, particularly in respect of the mechanical behaviour of fibres during dyeing, but a good deal has been accomplished in the past few years[8, 9], and I will endeavour to present as full a picture as possible.

1. MECHANICAL BEHAVIOUR

Before considering the effect of the influences which we have just mentioned, let us examine the mechanical properties of fibres more generally. If we take a fibre and apply force so as to stretch it, we can continue to do so until the fibre breaks. If this experiment is done under controlled conditions with an increasing force applied, we can measure at each stage the extension of the fibre which is produced. The force required to break the fibre under these controlled conditions and the extension which it has undergone at breaking point are usually regarded as characteristic properties of the fibre and are often quoted in technical literature. The main value of these "tenacity" and "extensibility at break" values in the present context is as a measure of serious damage having occurred, as for example in the overbleaching of cotton. In normal wet processing we shall be more concerned with forces considerably less than those required to break the fibre and correspondingly similar extensions. If, having applied a small force and stretched the fibre to a small extent, we then release the force and allow the fibre to relax, the extension which has been produced may be recovered to a greater or lesser extent, depending upon the nature of the fibre and the amount of the force originally applied. In this early part of the stress–strain curve, the extension produced usually bears a linear relation to the applied force, and the ratio of applied force to extension can be regarded as a characteristic property of the fibre— the *initial Young's modulus*. The recovery from these applied forces is the *elastic recovery*. Recovery does not necessarily occur immediately upon release of the stress, but is usually time-dependent; thus there may be short-term elastic recovery and long-term elastic recovery. We believe that in general the order of magnitude of most of the forces with which we are concerned in dyeing is similar to that in the region of initial modulus. In this preliminary treatment we have been concerned with tensile forces and extensions, but the behaviour of fibres when compressed, twisted, or bent follows a similar pattern.

We have already noted the action of water and other liquids which penetrate fibres upon the diffusion process. These liquids have a profound influence also upon the mechanical behaviour of fibres. The tenacity, extensibility at break, initial modulus, and elastic recovery may all be affected, the two latter being the more important effects from our present point of view. The effect is usually to reduce both the initial modulus and the elastic recovery compared with those of the dry fibre. Therefore under wet conditions fibres generally are more easily deformed by small forces and tend to remain so for a longer period. The extent to which the mechanical properties of the various fibres change on wetting depends upon the extent of penetration of the particular liquid used. In the case of an aqueous solution, it is related roughly to the water imbibition.

The effect of increase in temperature is similar in many ways to that of water, but we have as yet no ready means of predicting the effect in any particular case. Generally speaking, however, the mechanical properties of the more hydrophilic fibres are less affected by increase in temperature. The effect of increase in temperature whilst in the dry condition is of interest to us principally from the point of view of setting and mechanical finishing processes. More important from the strictly dyeing point of view is the combined influence of water or other wetting liquid and high temperature. The two effects apparently reinforce each other, so that a fibre whose mechanical properties are appreciably modified both by wetting and by heating in the dry condition to 100°c. may be considerably affected in boiling water. It must be emphasised that these changes, as a rule, do not represent any permanent change in the mechanical behaviour of the fibre. Unless a chemical change such as saponification of cellulose acetate, or a further physical change such as recrystallisation of cellulose triacetate, has taken place concurrently, the mechanical behaviour reverts to normal when the material is restored to normal temperature or is dried. However, if this restoration of normal conditions takes place whilst the material is under stress, there may be a spontaneous recovery on rewetting or reheating, unless the stress has been applied for a sufficiently long time to allow the strain to be released internally.

In this case, the material has been set in a modified form.

2. CHEMICAL BEHAVIOUR

In addition to these physical changes in the fibre, there is also the possibility of chemical changes, the mechanism of which is probably better known. Thus the extent of saponification under given conditions depends upon the precise type of cellulose acetate. Of the two major types, cellulose triacetate is saponified much more slowly than the secondary acetate. This is wholly due to the difference in rate of diffusion of the alkali into the fibre. The saponification of cellulose acetate results in a fibrous material of a different chemical structure, since the side-chains are saponified. The saponification of Terylene, however, results in chain rupture. The rate of diffusion of alkali into Terylene is so slow that the whole of the saponification takes place on the surface, which is dissolved away. This type of saponification does not affect the chemical structure of the material remaining: it merely dissolves a proportion of the fibre. With Terylene, the loss in weight may be quite serious at high temperatures under alkaline conditions. The effect of alkali on wool, particularly under reducing conditions such as are found in vat dyeing, is to dissolve the fibre, and these conditions are normally avoided. The effect of similar conditions on the regenerated protein fibres is only to swell the fibres to a greater extent than in water: the fibres have a very low Young's modulus under these conditions, and any damage which is caused is due to mechanical forces, the chemical structure being unchanged.

3. DYEING PROCESSES

The large differences in the physical behaviour of fibres are immediately apparent in the processes which we have adopted for dyeing. The high initial modulus of cotton, for example, allows processing of piece-goods to be conducted with little regard to the warpways tensions entailed. In both jigger dyeing and continuous dyeing processes this is advantageous, since the fabric can be more readily controlled in open width when under tension. Similar tensions applied to continuous-filament woven fabrics of viscose rayon or secondary cellulose acetate, which have considerably lower initial moduli, would produce considerable warpways extension. In the case of viscose rayon, this would be recovered to a large extent at a later stage, possibly during use, as fabric shrinkage; whereas internal relaxation of the acetate will take place, leaving a relatively stable extended fabric with modified handle. In order to prevent these effects, it is necessary to operate the machines with low warpways tension, and maintain control of the fabric by closer supervision or better mechanical devices.

Continuous-filament knitted fabrics, on the other hand, usually form satisfactory ropes, owing to the flexibility of this construction, and can be dyed in the winch machine. In this method of dyeing, warpways tension is much lower, and the main difficulties occur with the bending forces. In rope form, the fabric is necessarily subjected to these forces, and if the resulting strain is sufficiently relaxed internally during one cycle of the fabric, a crease results and the fabric tends to run in the same fold during the next cycle. This has two effects— permanent creasing of the fabric and consequent unlevel dyeing. The fibres which are most susceptible are those having a low initial bending modulus and a poor short-term elastic recovery at high temperature, viz. the cellulose acetate and acrylic fibres. The extent of the elastic recovery may depend to a large extent upon the length of time during which the bending force has been applied, and it is often advantageous to reduce this time by increasing the linear speed of the fabric over the winch. Even under the most advantageous conditions, the maximum temperatures at which cellulose acetate fabrics can be processed satisfactorily in rope form are 60°c. for the secondary acetate and 90°c. for unset triacetate. At the high temperature, usually close to the boil, which is necessary in the dyeing of acrylic fibres, the initial modulus is so low that even with the low warpways tension of winch dyeing, considerable fabric extension may result.

The behaviour of many fabrics during winch processing can be improved by a pretreatment in water, steam, or dry heat whilst the fabric is in open width. The object of this is to release the strains introduced during the processes of fibre manufacture, warping, sizing, and weaving, so that the yarn forms of the open-width fabric are the stable ones. To achieve this, the initial modulus of the fibre must be reduced and time allowed for the necessary internal relaxation processes to take place. With the thermoplastic fibres, this can be achieved by short-term high-temperature treatments, but in the case of wool the much longer process of crabbing is necessary, since changes in the cross-linked structure of the fibre must be allowed to take place. As a result of these treatments, we may achieve not only strain relaxation, but further rearrangements in the internal structure of the fibre, which result in a higher initial modulus of the fibre during the dyeing process. For example, the initial modulus of Tricel can be appreciably increased by a treatment in boiling water or steam.

Owing to the stresses applied during preliminary processes, yarns also are supplied to the dyer in a state of strain. For instance, nylon and Terylene continuous-filament yarns, which undergo drawing as part of the manufacturing process, and those viscose rayon continuous-filament yarns which have been dried in a state of tension, as in the normal continuous process, contain unrelaxed strain which when relaxed under suitable conditions causes a shrinkage which may be 6–10% or even more. If the dyer wishes to dye the yarn in package form, it is necessary to relax it before package making, otherwise when the viscose rayon yarn is wetted or the nylon and Terylene yarns are heated to dyeing temperature, the relaxation shrinkage will cause a tightening of the package structure, with reduced penetration of liquor and possible differences from one part of the package to another. The forces involved in these shrinkages may be so high as to tighten the packages to the former, from which

they cannot easily be removed. This property of shrinkage due to strain relaxation is currently being used in the preparation of high-bulk yarns from the acrylic fibres, the high-bulk effect coming from the combination of high-shrinkage and low-shrinkage fibres in the same yarn. Owing to the low initial modulus of the acrylic fibres at the temperature necessary for dyeing, extension of the fibres can readily occur sufficient to counterbalance the shrinkage. Great care must be taken to allow this shrinkage to take place without restraint and, after shrinkage has taken place, to prevent any longitudinal stress being applied to the yarns or fabrics whilst hot and wet, if the maximum bulk is to be obtained.

The dyeing of loose fibres and slubbing is usually carried out in machines with liquor flow, designed originally for cotton or wool. The capacity of the pump is usually high, so as to obtain a high rate of flow through the pack and thus to assist levelness of dyeing. The liquor exerts a pressure across the mass of fibres which depends upon the resistance to flow offered by this mass, and compresses it to an extent depending upon the moduli of the fibres concerned. Thus with fibres of high crimp, such as wool, which make a relatively open pack, the resistance to flow is low; hence the compressive force is low, and in spite of the relatively low modulus of wool, the resulting consolidation is only slight. This allows a high rate of liquor flow to be maintained, and the dyed material is in good condition for further processing. Less satisfactory results are often obtained when other fibres are dyed in this form, owing to the greater density of packing in the first instance and the lower moduli of the fibres concerned. Difficulties are experienced with viscose rayon and cellulose acetate, especially in the finer deniers, but the effect is most marked with the acrylic and regenerated protein fibres, which, owing to their very low moduli, cannot readily be dyed as tops in can-type machines, and are often severely compacted when dyed as hanked slubbing or loose staple in cage-type machines. In the latter, consolidation can, however, be minimised by reduction of pump capacity or restriction of flow [10].

* * *

My thanks are due to the Directors of Courtaulds Ltd. for permission to publish this paper; to Mr. John Boulton for his encouragement and helpful criticism; and to all those of my colleagues who assisted in the preparation of the paper and the exhibits.

RESEARCH LABORATORY
COURTAULDS LTD.
DROYLSDEN
MANCHESTER

(*MS. received 20th October 1958*)

References

1 Fern, A. S., J.S.D.C., **71**, 502 (1955).
2 Bradshaw, S. N., *Personal communication*.
3 Sutton, G. D., *J. Textile Inst.*, **42**, P 538 (1951).
4 Garrett, D. A., J.S.D.C., **73**, 365 (1957).
5 Walls, I. M. S., *ibid.*, **72**, 261 (1956).
6 ICI, *The Dyeing of Terylene Polyester Fibre* (Manchester: 2nd edition 1954), p. 5.
7 Marshall, W. J., J.S.D.C., **71**, 13 (1955).
8 Meredith, R., *The Mechanical Properties of Textile Fibres* (Amsterdam: North Holland Publishing Co. 1956).
9 Guthrie, J. C., *J. Textile Inst.*, **48**, T 193 (1957).
10 Meldrum, K., and Ward, J. S., J.S.D.C., **74**, 140 (1958).

Flameproofing of Textile Fabrics with particular reference to the Function of Antimony Compounds

N. J. READ and E. G. HEIGHWAY-BURY

Meetings of the London Section held jointly with the London Branch of the Clothing Institute in the rooms of the Royal Society, Burlington House, London, on 4th October 1957, Dr. T. H. Morton in the chair; and at the One-day Symposium on "New Information on Finishing Processes" held by the Manchester Section at the Manchester College of Science and Technology on 21st March 1958, Mr. J. W. Reidy in the chair

Some modern flameproofing processes are outlined, and the requirements of an ideal process discussed together with some methods of testing flameproofness and durability. The importance of ease of ignition as distinct from rate of burning as a fire hazard is referred to.

The action of antimony oxide in association with hydrogen chloride liberated at ignition temperature is examined, and an experimental demonstration of the mechanism of the flameproofing effect of antimony chloride is described. The preparation, application, and performance of oil-in-water emulsions of plasticised polyvinyl chloride are discussed, and evidence of possible side-effects of the composition and antimony oxide is supplied.

INTRODUCTION

Three durable flameproofing processes for textiles have reached the stage of commercial development in this country in recent years. *Proban*, sponsored by Albright & Wilson Ltd. and the Bradford Dyers Association Ltd., is based on tetrakishydroxymethylphosphonium chloride. *Lifeguard*, based on a combination of oxy compounds of titanium and antimony, has been developed in this country by Peter Spence Ltd. The most recent process to come on the market, which employs antimony oxide and a chlorinated compound, has been developed by Associated Lead Manufacturers Ltd.

The object of this paper is to discuss the function of antimony oxide in flameproofing without reiterating too much the information already very fully supplied by F. Ward [1]. Before proceeding to the main subject, it may not be out of place to sketch some background against which modern systems of durable flameproofing are developing.

By the middle of the nineteenth century most of the soluble salts now recognised as flameproofing agents had been used or suggested either alone or in

mixtures. The substitution of flannelette for flannel led to considerable activity in attempts to obtain a permanent flameproof treatment which would withstand launderings, and to this end Perkin obtained patents in 1903 and 1913 for treatments with sodium stannate and sodium aluminate [2].

During World War II there was great activity in the flameproofing field to meet military requirements, and advances were facilitated by the introduction of new chemical compositions. Recently, some awakening of public conscience has led to organised efforts in the newspapers to awaken the public to the dangers of fire, particularly as affecting the very young and the old. In the U.S.A., legislation controlling the sale of highly flammable fabrics was enacted in 1954.

In this country the British Standards Institution has recently published the findings of a committee which has been inquiring into *The Flammability of Apparel Fabrics in relation to Domestic Burning Accidents* [3]. A factor of flammability risk is the weight of the material. The rate at which materials of the same composition burn is inversely proportional to their weight per unit area.

Throughout the literature there is some confusion in the terms used: thus "fireproof", "flameproof", and "flame-resistant" are used, even to the extent of being interchangeable. However, the term *fireproof* should convey the meaning of total resistance to destruction by fire, such as is given by asbestos-like material. According to the above committee [3] a material which, although it does not withstand the action of fire, does not propagate flame after removal of the source of ignition should be termed *flameproof*. *Flame-resistance* characterises a material which does not burn readily.

Flameproofing processes have generally been developed for cotton fabrics, since the fire risks associated with these materials constitute a serious drawback, for many purposes, to their use in wearing apparel. Other cellulosic fabrics, such as linen, ramie, hemp, and jute, behave similarly to cotton, and among man-made fibres viscose rayon may be regarded as having approximately the same flammability as cotton.

TEMPORARY AND DURABLE FLAMEPROOFING

Flameproofing processes fall into two categories— temporary and durable— according to whether they will or will not withstand laundering. For some purposes treatments which are temporary, in the sense that they are not resistant to washing, are valuable, e.g. theatrical properties and materials which are not subject to washing. But for fabrics for wearing apparel or domestic use, such treatments can lead to a feeling of false security, and the emphasis must be almost as much on resistance to dry cleaning and laundering as on flameproofing.

IDEAL CHARACTERISTICS OF A FLAMEPROOFING PROCESS

The requirements of an ideal flameproofing process are numerous, but may be summarised as follows—

(1) A minimum "add-on", to avoid excessive increase in weight, is desirable
(2) Satisfactory handle of flameproofed fabric
(3) Ease of application— by no means the least important characteristic, because of its effect on cost of manufacture
(4) Good resistance to laundering and dry cleaning
(5) Freedom from detrimental action on the material
(6) No decrease of vapour transmission such as might be caused by filling the pores in the fabric
(7) No harmful physiological effects
(8) The treatment should not increase *afterglow*, which is the flameless combustion of the residual char and sometimes of the unburnt material.

With such a formidable list of requirements for an ideal process it is improbable that they will all be fulfilled by any one process, and, as in the majority of technical developments, no doubt some compromise will be found to be acceptable.

TESTING OF FLAMMABILITY

In the vertical burning test [4] it is not easy to assess the rate of flame spread visually. The vertical test undoubtedly has the merit of most closely approaching the conditions usually occurring with the ignition of apparel. Owing to the uprush of air caused by heat a very intense flame is developed. In tests carried out in our laboratories it has occasionally been found that a material not ignited in the 45° test [5] will burn vigorously once a substantial sample is well alight in a vertical position. In researches directed towards estimating fire hazards little attention appears to have been paid to ease of ignition. Possibly ease of ignition is closely associated with rate of burning, which is more easily determined, but it may well be that ease of ignition is of greater importance. Once a garment is well alight, it would appear only of secondary importance, except in the case of extremely flammable material, at what rate it burns, if in the panic the wearer fails to take appropriate steps to extinguish the flame. The slower-burning fabrics will, of course, give more opportunity of controlling the fire provided that immediate action is taken.

TESTING RESISTANCE TO WASHING AND DRY CLEANING

The problem of testing resistance to washing is considerably more difficult than testing flameproofing. Resistance to dry cleaning can no doubt be fairly easily determined, because the solvents and techniques used are well known and their action on any flameproofing compounds can be readily ascertained. Wash resistance is much more difficult to assess, because the methods used domestically are almost infinitely variable both in mechanical handling and in the nature and quantity of the chemicals used. The objective of a durable flameproofing process must be to provide a treatment which will retain its flameproof character

throughout the life of a garment, but the length of this must vary with the habits and views of the wearer.

In tests on fabrics flameproofed by the Antiflamm process, developed by Associated Lead Manufacturers Ltd. together with Horrockses Spinners & Manufacturers Ltd., it has been found that, although it is not adversely affected by boiling with soap and soda, the fabric should not be boiled with synthetic detergents, as some of these compounds at boiling temperatures tend to affect the flame-resistant properties. At lower temperatures no ill effects occur even with detergents. This might be expected from the chemical resistance of polyvinyl chloride, one of the components.

A more realistic test is one in which there is much mechanical attack, which might be expected to separate the impregnating resin from the fibre. Such conditions, which are drastic, are found in a domestic washing machine, and in our trials a Hoover machine has been utilised. The most severe treatment recommended by the makers for this appliance is a wash of 4 min. at 60°C., the amounts of soap and soda being adjusted to give a small area of lather on the surface whilst running. Using the prescribed method, a large number of sample materials have shown no appreciable loss of flameproofing after 100 launderings.

Other samples have withstood weekly laundering at a commercial laundry for a period of 10 months to date, without apparent loss of flameproofness.

Plasticised polyvinyl chloride compositions are very resistant to the solvents used in dry cleaning. Prolonged extraction with perchlorethylene or white spirit, the most commonly used solvents, has been found to have no effect on fabrics flameproofed by the Antiflamm process.

ANTIMONY IN FLAMEPROOFING

Among the processes utilising antimony oxide, the Lifeguard process is unique in being based on precipitation in the fibre of an oxy compound of titanium together with the antimony oxide. The latter is normally much less effective in the absence of a hydrogen chloride donor, with which it provides antimony chloride upon ignition.

THEORIES OF THE FLAMEPROOFING OF CELLULOSE

Theories which attempt explanation of the mechanism of flameproofing may be classified under four headings—

(1) *The Chemical Theory*

The evidence in favour of this theory is based on work by Ramsbottom and Snood, Mety, Serebrennikov, Palmer, and Richardson, who observed that effective chemicals alter the course of decomposition of cellulose, favouring the formation of lesser amounts of flammable tars and gases which cause flame and increasing the amount of non-volatile carbonaceous materials [6]. Ward [7] has put forward a new theory for the basic mechanism of the burning and flameproofing of fabrics.

(2) *The Coating Theory*

This theory explains certain treatments that produce an impermeable glassy layer or skin on the fibre surface at ignition temperature, e.g. borax-boric acid mixtures.

(3) *The Gas Theory*

It is suggested that chemicals which yield inert gases on heating may function as flame-retardants by reducing the concentration of oxygen in the atmosphere to a point at which flame propagation ceases.

(4) *Thermal Theories*

Two concepts are prevalent— the first that the heat input may be dissipated by endothermic changes in the retardant; the second that heat may be conducted away from the fibres.

Antimony oxide, although not a very effective flameproofing agent in the absence of hydrogen chloride, was used extensively during World War II (10,000 tons per annum), as it was found to be sufficiently effective to prevent ignition of camouflage scrim by gun flash. Under these conditions its effect may be explicable by theories (2) and (4), because it has the unusually low melting point, for an oxide, of 656°C. Where antimony oxide is associated with a source of hydrogen chloride available at ignition temperature, theories (1) and (3) afford the most probable explanations of its effectiveness.

ANTIMONY OXIDE IN ASSOCIATION WITH A HYDROCHLORIC ACID DONOR

Antimony forms three oxides. Antimony pentoxide Sb_2O_5 is said to react with cellulose, rendering the treated material insoluble in cuprammonium solutions [7]. The tetroxide Sb_2O_4 is not readily available on a commercial scale, and only the trioxide Sb_2O_3 fulfils the requirements of the type of flameproofing process involving a chlorine compound.

It is desirable to use an antimony oxide of small particle size, and this is best obtained in a fumed product having an ultimate particle size of 0·25–1·0 μ. Coarser products, having lower opacity, can be prepared and have advantages in retaining translucency in some types of plastic sheet flameproofing, but their disadvantages far outweigh their advantages when used in impregnating compositions for textiles.

Although antimony oxide alone has only a limited effectiveness as a flameproofing agent, antimony oxychloride has for a very long time been recognised as an effective flame-retardant; but it cannot be used to flameproof textiles, because it easily hydrolyses to yield hydrochloric acid, which destroys the fabric, particularly cottons.

With the commercial production of chlorinated organic compounds such as polyvinyl chloride, chlorinated paraffins, etc. which yield hydrogen chloride when decomposed by heat, much work has been done with the object of utilising the characteristics of these materials in conjunction with antimony oxide to produce antimony chloride *in situ* only at the ignition temperature of cellulose.

Antimony chloride may well function in two ways— firstly by reacting with cellulose to alter the course of thermal decomposition, and secondly by forming a heavy vapour tending to extinguish flame. It melts at 73°C., at which temperature it exerts a powerful dehydrating effect on cellulose. It boils at 223°C., and the vapour, as well as having a dehydrating effect, is very heavy, and may well have a blanketing effect on flame.

The extremely effective performance of antimony chloride certainly depends on the fortunate circumstances of its low melting and boiling points, since a zinc oxide–chlorinated body composition is only slightly effective, although zinc chloride, probably hydrated, is said to be an effective flame-retardant when used to impregnate cellulosic materials. Its effectiveness in the zinc oxide–chlorinated body system may well be due to the melting point of anhydrous zinc chloride being only a little below the ignition temperature of cellulose, and its boiling point as high as 732°C.

The decomposition of a chlorinated body and the formation of antimony chloride from the oxide at the ignition temperature of cellulose may occur in several ways. There may be direct formation of antimony trichloride, or it may be produced by the action of heat on an antimony oxychloride, which may be the compound first formed. Antimony oxychloride begins to decompose at 170°C., and decomposition ceases at 280°C., when the composition is $Sb_4O_5Cl_2$, a pentoxydichloride. The latter compound melts without decomposition, but decomposition begins at 320°C., and is complete at about 700°C.

In the complex conditions of a burning fabric it may be impossible to determine which of these reactions occur, but in all cases the end-products would appear to be antimony trichloride and antimony oxide in accordance with the following equations—

A $Sb_2O_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2O$ (b.p. 223°C.)

B $Sb_2O_3 + 2HCl \rightarrow 2SbOCl + H_2O$ (i)

$5SbOCl \rightarrow SbCl_3 + Sb_4O_5Cl_2$ (decomp. 170–280°C.) (ii)

$3Sb_4O_5Cl_2 \rightarrow 2SbCl_3 + 5Sb_2O_3$ (decomp. 320–700°C.) (iii)

A few very simple experiments help to throw light on the flameproofing mechanism. Samples of untreated winceyette and the same material after treatment with antimony oxide and plasticised polyvinyl chloride were heated in air in an oven for 5 min. at 200°, 250°, and 280°C.—

At 200°C. the untreated and treated materials both tended to become brown, but did not differ markedly in appearance.

At 250°C. the untreated material became light brown, but still retained its fibrous character. The flameproofed material became dark brown and brittle.

At 280°C. the untreated material was still fibrous and extremely flammable. The treated fabric assumed the character of a brittle black char, which had no flaming property, but tended to be destroyed by flameless combustion. The char represented 37% of the fabric and contained 4·7% Sb_2O_3, indicating that 80% of the Sb_2O_3 originally present had been converted to antimony chloride and vaporised.

In all three experiments heavy fumes were evolved from the treated materials, and these fumes were capable of extinguishing a flame. The chlorine present in the resin and plasticiser is greatly in excess of that required by the antimony, and is liberated as hydrogen chloride at a temperature of about 200°C. At ordinary ironing temperatures no fumes are evolved.

The fumes are mainly derived from vaporisation of the plasticiser, which in these experiments was a mixture of dioctyl phthalate and a chlorinated paraffin, Cereclor. A further experiment showed that the fumes from the boiling plasticiser are flammable, but if antimony oxide is mixed with the plasticiser before boiling, the fumes not only are non-flammable, but are capable of extinguishing a flame.

The ignition temperature of cellulose is said to be of the order of 320°C., and Ward recorded 700°C. as the ignition temperature [7] of cotton web. It is clear, therefore, that well below these temperatures an interaction between cellulose and antimony chloride takes place which converts the cellulose to a non-flaming compound. At the same time flame-extinguishing fumes are evolved which reinforce the non-flaming conditions of the system.

Whether antimony chloride is formed directly from the hydrogen chloride liberated from the chlorinated compound, or whether an oxychloride is first formed and decomposed below 280°C., cannot be definitely stated, but in either reaction antimony chloride in ample quantity to alter the cellulose decomposition process is formed well below ignition temperature [8].

ANTIMONY OXIDE–POLYVINYL CHLORIDE EMULSION TYPE OF FLAMEPROOFING

A very extensive investigation of methods of flameproofing with aqueous emulsions of antimony oxide and a chlorinated substance was carried out in the U.S.A. during the war and is fully described in R. W. Little's comprehensive report [6]. The conclusions drawn were that a water-in-oil emulsion was better than an oil-in-water emulsion. The chlorinated compound was usually a chloroparaffin, but some chlorinated vinyl compounds were used. In all cases the latter were dissolved in a volatile solvent.

In 1952 the Treesdale Laboratories obtained patents in the U.S.A. for an oil-in-water emulsion of a plasticiser, polyvinyl chloride latex, and antimony oxide [9]. In 1953 an investigation was commenced in our Central Research Laboratories, with the object of developing a process for flameproofing textiles based on the use of antimony oxide.

Experiments showed that the proportion of plasticiser to polyvinyl chloride could be greatly increased by using a mixture of a chlorinated paraffin of low chlorine content together with the primary inflammable plasticiser, and this much

improved the handle of the treated fabric without detracting from its flameproofness. Improved methods of emulsification and stabilisation of the plasticised emulsion gave stability equivalent to 3–5 months' storage, and incorporation of the antimony oxide in the oil phase. instead of in water, greatly improved the suspension of the pigment. Frothing was almost entirely suppressed by the addition of a foam suppressor, the silicone types being most effective. A typical composition of an emulsion now in use, Timonox Flame-retardant Emulsion, is given in Table I.

TABLE I

Composition of Typical Flame-retardant Emulsion

	Parts by wt.
EMULSION	
Cereclor 2 (a chlorinated paraffin)	362
Dioctyl phthalate	362
Sodium carboxymethylcellulose (2% soln.)	100
Emulsifying agent	16
Water	600
Antimony oxide	364
Polyvinyl chloride latex	1500
Silicone antifoam	1·0

Specific gravity of emulsion 1·2

CURED RESIN	(%)
Plasticiser	38·8
Antimony oxide	19·4
Polyvinyl chloride	41·8

METHODS OF APPLICATION

The antimony oxide emulsion method of flameproofing fulfils one of the requirements of a successful commercial process in that it can be readily applied with normal dyehouse machinery.

The liquor is applied to the fabric by padding, and any surplus is expressed by adjustment of the nip to give a desired wet "add-on" which is a direct function of the final dry "add-on". The treated fabric is then dried, and cured at 120–140°C. for 2–4 min. Washing and treatment with an appropriate softening agent may then be carried out if necessary in conventional plant used for this purpose.

In special circumstances the emulsion may be applied by brush or spray. For example, the hessian backing of a carpet can be flameproofed after manufacture by spraying or brushing the emulsion on to the reverse side, subsequently drying and curing. However applied, the emulsion is absorbed by the fibres, and thus a continuous surface coating of the fibre is formed.

CONDITIONS INFLUENCING ADD-ON

Although all durable processes depending on a resin bonding substantially increase the weight of the treated fabric, the antimony oxide–chlorinated body process tends to increase strength (see below), so that the add-on can to some extent be countered by reduction in the initial weight of the fabric. This has been most satisfactorily achieved with winceyette, and can no doubt be applied to other materials when desired.

The add-on necessary for complete protection varies with the surface and the weave. For example, with 14-oz. duck a 20% add-on is quite sufficient, increasing to 30% for 6-oz. drill, to 45% for winceyette, and even more may be required for fine cotton nets. The cost per square yard, of course, is not necessarily higher when the add-on increases.

These figures represent the add-on necessary for *complete* non-ignition by any test and retention of the flameproofness throughout repeated washings during the lifetime of the fabric.

INFLUENCE OF FLAMEPROOFING ON STRENGTH

Since in this process the fabric is at no time subjected to attack by acids, no tendering occurs. The impregnation with a soft flexible resin composition having itself appreciable strength actually increases the fibre tensile strength. This may not always be reflected in tear strength on account of some lack of slip between the woven fibres, but the loss, if any, is too small to be of significance. The tensile strengths of a number of fabrics, determined on an Avery constant-rate-of-loading machine, are shown in Table II.

TABLE II

Tensile Strengths of Flameproofed Fabrics

(Test strips 2 in. × 7 in.)

Material	Treatment	Add-on (%)	Tensile Strength (lb./sq.in.)	Increase (%)
6-oz. Rayon–cotton	Untreated		151	
	Treated	46	192	27
12-oz. Cotton twill	Untreated		141	
	Treated	43	164	16
Chintz	Untreated		108	
	Treated	43	117	8
Rayon–cotton winceyette	Untreated		134	
	Treated	38	136	1·5
Twill-weave cotton winceyette	Untreated		42	
	Treated	50	49	16

INFLUENCE ON COLOUR

Antimony oxide is a pigment of relatively high opacity, so that some effect on coloured fabrics is unavoidable, but it becomes embarrassing only in the flameproofing of materials having large areas of deep colour. It also has a delustring effect on certain fabrics. Probably this can be mitigated by increasing the strength of the colour, or possibly by flameproofing before dyeing. No masking occurs with pastel colours and prints of small highly coloured designs.

The treatment has no adverse effect on the life of vat or direct dyeings and in some cases appears to afford some protection against fading during laundering.

INFLUENCE ON HANDLE

The maintenance of an acceptable handle is probably one of the most difficult problems encountered in durable flameproofing. The original experiments with antimony oxide–polyvinyl chloride impregnation were confined to fabrics such as are used in industrial clothing, where some stiffness is permissible or even desirable. Later the work was extended to a variety of fabrics, particularly to winceyette, where soft handle is of

primary importance, and modifications in the process led to the production of flameproofed materials which are regarded as satisfactory.

The stiffness associated with a resin impregnation process of this kind does not appear to depend so much on any stiffness of the impregnating compound itself as on the cementing of the fibres together at their points of contact. Thus materials of open weave give much more satisfactory results than those of a very close texture. For example, flameproofed twill winceyette with a 45% add-on is hardly distinguishable except in weight from the untreated material, while a more closely woven plain winceyette cannot be obtained with the same handle, although it is still perfectly wearable. Cotton and cotton–rayon drills show stiffening, but improve with washing to almost their original texture without loss of flameproofness. Very satisfactory results are obtainable with cotton nets and with those materials with which a certain crispness is required. This finish, of course, is fast to washing. The crispness can best be obtained by incorporating starch in the emulsion.

The treatment does not fill the pores in the fabric, so no reduction in vapour transmission is detectable and permeability is unimpaired.

TOXICITY

Two aspects must be considered in this connection. Firstly, dermatological effects of wearing flameproofed clothing next to the skin, and secondly toxicity from the ingestion of the flameproofing addition if the fabric is chewed by children.

Exhaustive tests by the Consulting Dermatologist to the Manchester Chamber of Commerce Testing House have disclosed no risk of skin irritation.

The soluble salts of antimony such as tartar emetic are toxic, but the insoluble compounds such as antimony oxide are harmless, since they will not enter the system through solution in the gastric fluids. As a further precaution the Medical Research Council Burns Unit has demonstrated the lack of any substantial extraction of antimony oxide by a series of actual chewing tests on flameproofed materials.

With regard to antimony trioxide, C. W. Price[10] has stated—

> Antimony oxide is non-toxic and is classified as such. The non-toxicity is proved by the absence of any effect on the health of workmen exposed to fumes of antimony trioxide over very many years. In factories engaged in the manufacture of antimony oxide no poison regulations are applied or needed.

CONCLUSION

It must probably be admitted that no flameproofing process has yet been discovered which fulfils all the ideal requirements. Nevertheless, it appears that there are a few which have most of the properties demanded. The antimony oxide–chlorinated compound process includes a reasonably low cost, ease of application, non-toxicity, and the ability to withstand dry cleaning and laundering during normal expectation of the life of the garment. While not applicable to all types of material, it can be used for a wide range of fabrics without undue effect on handle or colour.

* * *

Thanks are due to the Directors of Associated Lead Manufacturers Ltd. for allowing publication of this paper and to their Central Research Laboratories, Perivale, for their work in connection with it.

FLAME-RETARDANTS DEPARTMENT
ASSOCIATED LEAD MANUFACTURERS LTD.
138 ROYAL EXCHANGE
MANCHESTER 2

(*MS. received 11th November 1957*)

References

1 Ward, F., J.S.D.C., **71**, 569 (1955).
2 Perkin, W. H., *BP* 24,222 (1903) and 17,814 (1913).
3 British Standards Institution, *PD* 2777 : 1957 (London).
4 Idem, *B.S.* 2963 : 1958.
5 American Society for Testing Materials, *Method of Test for Flammability of Clothing Textiles*, D 1230–52 T (Philadelphia).
6 Little, R. W. (editor), *Flameproofing Textile Fabrics* (New York: Reinhold Publishing Corpn. 1947), p. 77.
7 Ward, F., J.S.D.C., **71**, 576 (1955).
8 Idem, *ibid.*, **71**, 575, 577 (1955).
9 Treesdale Laboratories, *USP* 2,518,241, 2,591,368.
10 Price, C. W., *J. Oil & Col. Chem. Assocn.*, **26**, 105 (1943).

Discussion

MANCHESTER SECTION

Mr. L. HOLLAND: What kind of afterglow times can be expected after this kind of flameproof treatment?

Mr. HEIGHWAY-BURY: This depends on the material treated and the amount of add-on. In most cases there is no afterglow, or very little, and where there is afterglow this does not spread beyond the charred area. If a requirement for afterglow time is specified, say 2 sec., an additive which eliminates afterglow, such as antimony phosphate, can be supplied.

Mr. A. H. LEVIN: Carpets in public places often have cigarette-ends stubbed out on them. Would the flameproofing treatment be of any help in reducing the resultant damage?

Mr. HEIGHWAY-BURY: No. There would still be charring of the portion of the carpet where the live cigarette-end drops. Of course, if there were any ignition, this would not spread beyond the area of the source of ignition.

Mr. J. W. LONGLEY: Could tritolyl phosphate or trioctyl phosphate be used in place of dioctyl phthalate in compositions for flameproof treatments?

Mr. HEIGHWAY-BURY: The choice of plasticiser is determined by many factors, such as toxicity, influence on handle, cost, and the application properties of the emulsion, and those plasticisers are adopted which would give the best compromise among all these requirements.

Mr. D. R. WOOD: Will the speaker describe the method of laundering the treated fabrics? Is the finish fast to modern detergents, especially those containing sequestering agents?

Mr. HEIGHWAY-BURY: As already mentioned, the fabrics were subjected to weekly commercial laundering for a period of 10 months. In addition, a separate series of tests showed that the fabric

withstood detergents as specified in the proposed British Standard (B.S.I. Technical Committee G 5).

Dr. G. McLEAVY: The samples handed round which have been heated illustrate the flame-proofing properties but also show the increased charring characteristic of treated cloths. Has any difficulty been experienced with domestic ironing of treated cloths due to increased browning, and does this tendency limit use in industrial fields at high temperature?

Mr. HEIGHWAY-BURY: The temperatures used for the samples in question were much higher than ordinary ironing temperatures.

Dr. McLEAVY: What is the toxicity of antimony chloride?

Mr. HEIGHWAY-BURY: Although, since antimony trichloride is listed as a Schedule 1 poison under the Pharmacy and Poisons Act 1933, there would be some risk if it were swallowed either in the solid form or in solution, as far as the vapour is concerned it would be expected to react immediately it came into contact with moisture or moist air to form insoluble, relatively innocuous substances. Any possible danger from inhalation of antimony compounds would be small compared with the fire hazard which it is intended to overcome.

Dr. R. S. HIGGINBOTHAM: Does any removal of plasticiser, with resultant stiffening of the fabric, occur during dry cleaning?

Mr. HEIGHWAY-BURY: It is a remote possibility, but on materials we have so far treated (i.e. winceyettes and drills) this effect is negligible.

Mr. G. COE: Has any work been carried out on flameproofing union fabrics, particularly nylon–cotton union, by the Antiflamm process? Whereas nylon itself melts and forms droplets which extinguish a flame during the vertical strip test, when this fibre is present in admixture with cotton the material continues to burn. This is also the case even when the usual borax–boric acid has been applied.

Mr. HEIGHWAY-BURY: We have tried, by using the Timonox system, to flameproof nylon warp–cotton weft upholstery fabrics, but without success.

Flame-resistant Finishing of Cellulosic Fabrics with Phosphorus-containing Resins

J. R. W. PERFECT

Meetings of the Scottish Section held at the St. Enoch Hotel, Glasgow, on 21st January 1958, Mr. W. G. B. Grant in the chair; and at the One-day Symposium on "New Information on Finishing Processes" held by the Manchester Section at the Manchester College of Science and Technology on 21st March 1958, Mr. J. W. Reidy in the chair

Methods of using phosphorus-containing compounds to produce durable flame-resistant finishes on cellulosic fabrics are discussed. Reference is made to finishes based on the use of amine–phosphate–formaldehyde resins, esterification methods, phosphorylamide compounds, tetrakishydroxymethylphosphonium chloride (THPC) resins, triallyl phosphates, and aziridinylphosphines. Particular mention is made of the commercially successful Proban finish, which is based on the use of THPC. A brief summary is given of suggested mechanisms for the flame- and glow-proofing action of phosphorus compounds.

It has been known for many years that certain phosphorus-containing compounds can be applied to cellulosic fabrics to make them resistant to burning. As long ago as 1786 [1] ammonium phosphate was recommended for this purpose, and today it is still widely used in treatments for textiles and wood. To a lesser extent, acid sodium phosphates have been used alone or in mixtures with other compounds, and numerous other phosphorus-containing substances have been suggested from time to time.

All finishes based on phosphorus-containing compounds have one common property: they make the fabric resistant to smouldering, and even if insufficient finish is applied to prevent the fabric from burning, the residue will not be ash but a black char, a skeleton of the fabric, which is extremely resistant to prolonged fierce heating. Many compounds not containing phosphorus can be used to reduce the flammability of cellulose. but very few are effective also in preventing smouldering or afterglow. These few are for other reasons not commonly used or not as efficient as the phosphorus compounds, and it can be said that as a flame and glow proofer phosphorus holds a unique position.

Finishes based on soluble phosphates are not fast to washing, and it is only natural, therefore, that efforts should have been made to obtain more permanent effects by fixing the phosphorus on or in the fabric. The aim of this paper is to review and discuss some of these efforts to achieve permanency. In recent years there has been considerable activity in the field of phosphorus finishes, and this review is by no means comprehensive. However, it is intended to try and indicate by example most of the main lines of approach to the problem. As far as can be ascertained, all the methods which have reached some measure of commercial development are mentioned.

To conclude, a brief summary is given of theories relating to the mechanism of flameproofing and glowproofing in relation to phosphorus finishes.

1. AMMONIUM PHOSPHATE–DICYANDIAMIDE–FORMALDEHYDE

One of the first attempts to obtain a wash-fast phosphorus-containing finish involved the use of

ammonium phosphate together with a dicyandiamide–formaldehyde resin. A mixture of the two components was applied to the fabric, which was dried and baked to polymerise the resin. Unfortunately, at the baking temperature the ammonium phosphate decomposed, and the phosphoric acid liberated caused excessive tendering of the fabric. An ingenious modification to this method to avoid acid tendering was proposed by Bowen *et al.*[2]: they applied the ammonium phosphate–dicyandiamide–formaldehyde mixture to the cloth, and then precipitated the resin by treatment with alkali. Subsequent drying and heat-curing caused polymerisation of the resin without excessive tendering of the fabric. Finishes obtained by this method are resistant to water and mild washing, but not to hot soaping. However, the process has been used commercially to a limited extent for upholstery fabrics.

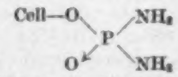
2. UREA–PHOSPHATE METHOD

The second approach to the problem of wash fastness was to try and combine the phosphorus with cellulose.

In the early 1930s a considerable amount of work was carried out on the formation of cellulose phosphate, but although this ester was found to be non-inflammable, it had such low strength that it was unsuitable as a textile fibre. It was not until 1949 that methods were devised to enable cellulose to be partially esterified without excessive loss in strength. Joseph Bancroft & Sons Co.[3] in America developed a treatment using urea and phosphoric acid, and later Courtaulds Ltd.[4] in this country suggested that the use of cyanamide with phosphoric acid would give a more efficient reaction with less tendering of the fabric. Subsequently, improvements have been claimed using other amines such as guanidine and dicyandiamide with the various phosphoric acids or their acid salts. Altogether a great deal of work has been carried out on these processes and on investigations of the reactions involved[5–10].

In all the methods, the fabric is padded in the aqueous reaction mixture, then dried, heat-cured, and finally washed off. The salt of the ammonium or nitrogenous base with the cellulose ester is formed, and the degree of esterification is generally in the region of 10–15% and the N/P ratio about 1·0. Treated fabrics are rather brittle and show considerable loss in strength. The addition of formaldehyde to the reaction mixture improves the strength of the finished cloth, but further reduces extensibility. Good flame and glow resistance are obtained and the effect is fast to water, but with repeated soap washing the fabrics gradually become inflammable. This is apparently due to the fact that the cellulose ester acts as a base-exchange material and forms the sodium salt (or with hard water the calcium salt). These metal salts of the ester are not flame-resistant. Rinsing with dilute ammonium chloride forms the ammonium salt of the ester and restores the flame-resistance—

It has been suggested[9] that prolonged heating of the ammonium salt forms the diamidophosphate, which is more stable to hard water and mild washing—



Cellulose diamidophosphate

Other modifications to the urea–phosphate method have been proposed to reduce the ion-exchange effect. One of these uses a mixture of melamine or diguanidine pyrophosphates with methylolmelamine or urea[11].

All the cellulose phosphate finishes, however, whether resistant to mild washing or not, are completely hydrolysed by hot alkaline scouring to cellulose and acid salts.

Banflam (Bancroft), Pyroset (American Cyanamid), and Pyrovatex (Ciba) are commercial finishes believed to be based on esterification procedures.

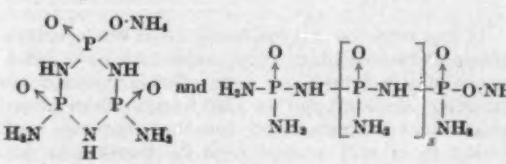
3. PHOSPHORYLATION WITH AMINATION

Other methods of combining phosphorus with cellulose have been proposed. For example, Thomas and Kosolapoff[12] have suggested direct phosphorylation with phosphoryl chloride, followed by amination, and Reeves, McMillan, and Guthrie[13] have suggested phosphorylating aminised cotton. These methods have theoretical rather than practical interest, and as far as is known no commercial processes have been developed.

4. PHOSPHORYLAMIDE METHOD

By reaction of phosphoryl chloride with ammonia a phosphorylamide can be made as a white powder containing about 34% P and 34% N and very soluble in water (60%) to give a solution of pH 8 (2% soln.).

Two possible structures have been suggested[14] for the product—

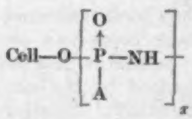


Methods of applying and fixing this product to cellulose have been patented[15].

In a recommended application a solution of 20–25% strength was applied to fabric with a wet pick-up of about 80%. The cloth was dried, and then cured at 150°C. for 5 min., when some 95% of the phosphorylamide was fixed. The cloth was then given a mild wash and aftersoftened: 12·4% add-on was obtained, corresponding to 3·6% P. It appears that the fabric so treated had good flame-resistance, fast to repeated mild washing and with no ion-exchange properties. However, considerable loss in tear strength was reported.

A freshly prepared phosphorylamide must be used because, on ageing, hydrolysis to ammonium phosphates can occur, and these cause tendering of the cellulose at curing temperatures. It is suggested

that during curing of this finish, not only does polymer build-up occur, but also some cross-linking—



If $x = 4$, A represents approx. 2 $O{\cdot}NH_4$, 1 OH, and 1 NH_2, but the exact composition of the final product will no doubt be influenced by the severity of cure.

This finish is marketed as Flame Retardant PA (Monsanto), but how far the process has been adopted commercially is not known.

5. AMINE–PHOSPHATE–FORMALDEHYDE COMBINATIONS

Many attempts have been made to fix combined phosphorus on cotton with thermosetting resins. An early method was due to Pollack [16], who suggested condensing *in situ* a phosphoric acid with urea or melamine and then fixing the deposit with urea- or melamine-formaldehyde resin. In a later modification, the double treatment was condensed into a one-bath process [17]. Pingree and Ackerman [18] applied a resin precondensate made by reaction of guanyl urea phosphate with formaldehyde. It would appear that these and similar methods patented in the late 1940s and early 1950s had limitations, because, as far as can be ascertained, none has been developed commercially. Probably the finishes were not fast to repeated washing, particularly hot alkaline washing, and certainly there would be problems associated with handle and strength.

6. THPC FINISHES

In 1953 Reeves and Guthrie [19] in America discovered that tetrakishydroxymethylphosphonium chloride (THPC) would react with aminised cotton to produce flame and glow resistance fast to boiling caustic alkalis. THPC was first made in 1921 by Hoffmann [20] by reaction of phosphine with formaldehyde in hydrochloric acid solution—

$$PH_3 + 4HCHO + HCl = (CH_2OH)_4PCl$$

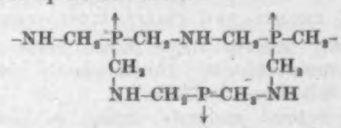
Reeves and Guthrie [21] soon showed that flame-resistant finishes with excellent fastness to washing could be obtained on ordinary cotton by applying THPC together with urea and a methylolmelamine. A typical finish of this type was made up as follows—

(*a*) 1868 g. THPC was dissolved in
1800 g. Water and
388 g. Triethanolamine added.

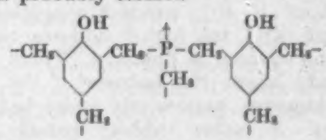
(*b*) 1069 g. Trimethylolmelamine and
1114 g. Urea were dissolved in
5062 g. Water.

These two solutions were mixed and applied to an 8-oz. cotton fabric to give a wet pick-up of about 76%. The fabric was dried at 85°c., baked at 142°c. for 4½ min., and washed with cold water and then hot detergent solution before final rinsing and drying. The finished fabric contained 16·6% resin, which was resistant to repeated washing and dry cleaning.

To appreciate why finishes based on THPC are so fast to washing, it is necessary to examine the chemistry of THPC itself. It is a hygroscopic crystalline, solid, extremely soluble in water and alcohols but insoluble in most organic solvents. It reacts with compounds with which aqueous formaldehyde reacts [22]. Thus under acid conditions with primary and secondary amines it can form compounds varying from water-soluble monomers to insoluble hard solid polymers, which are thought to be built up in this fashion—



With ammonia THPC readily forms an insoluble white polymer, and with phenols it forms polymers similar to phenol-formaldehyde polymers. For example, with phenol itself the following linkage is probably formed—



It will be noticed that polymers built up from THPC do not contain any P–O or P–N linkages. It is thought that the stability of these polymers to hydrolysis is due to the absence of these linkages and to the presence of P–C–N linkages.

The experimental work of Reeves and Guthrie has been followed up in England by Albright & Wilson Ltd. and the Bradford Dyers' Association Ltd. working conjointly, and a commercial finish has been developed [23]. This is the Proban anti-flame finish, which is now being applied in this country and overseas by textile finishers under licence from Proban Ltd. Considerable quantities of fabrics of various types have been processed, and these are being used for a wide range of purposes— workers' protective clothing, aircraft construction, filter cloths, furnishings for public transport and buildings, welders' screens, children's night and dress wear, and electric blankets. The Proban finish is basically a thermosetting resin finish, and treated fabrics have the properties associated with this type of finish. Because of the relatively large amounts of resin which are applied, the influence of fabric structure on finished properties is more pronounced than is the case with the average crease-resist finish.

The handle of treated fabric is generally affected to the extent that the fabric becomes fuller, but the firmness can be controlled from very soft to stiff according to requirements. Tensile strength is generally little affected or slightly reduced; tear strength is almost invariably reduced to an extent comparable with the effect of a normal resin finish. Fabrics treated with THPC resins seem to have remarkable resistance to rotting. Whereas untreated cotton is almost completely rotted away after soil burial for one month, treated fabrics show

no loss in strength after six months. Fabrics which are used for clothing have added advantages when treated with THPC resins: they show increased resistance to shrinkage and greatly improved recovery from wet creasing, so that with suitable fabric constructions good drip–dry minimum-iron properties can be obtained; there is also evidence that they are more resistant to repeated washing and wearing than untreated fabrics.

More recently, a commercial THPC finish, Pyroban (E. F. Drew & Co. Inc.), has been developed in the U.S.A., but what progress has been made with this is not known.

7. BROMINATED TRIALLYL PHOSPHATE

Recently efforts have been made to use phosphorus-containing thermoplastic resins to produce anti-flame finishes.

One method suggests using a brominated triallyl phosphate polymer. The triallyl phosphate is partially polymerised in organic-solvent solution or emulsion form using benzoyl peroxide as a catalyst. This can then be brominated and applied to fabric, or applied to fabric and brominated *in situ*[24]. Some 10–40% solids are applied to the fabric, and with the higher add-ons reasonable fastness to washing is obtained. There must be some doubt about the fastness of the bromine content, however, particularly under hot alkaline conditions. A rather rubbery handle may be obtained with the finish, although plasticisers can be used to counteract this to a limited extent. Fabric strength is not appreciably affected.

The disadvantages of this method would appear to be that the cost of raw materials is high, and preparation of the polymer is a rather laborious step-by-step procedure.

8. BROMOFORM–TRIALLYL PHOSPHATE

In another thermoplastic system, the use of an aqueous emulsion polymer of bromoform and triallyl phosphate (BAP emulsion) is suggested[25].

The preparation of the polymer plays an important part in the effectiveness of the finish. Either a 33% or a 40% emulsion can be made by the following method—

	40%	33%
Triallyl phosphate	236	189
Bromoform	164	132
Polyvinyl alcohol (medium viscosity)	8	6
Sodium bicarbonate	32	24
Potassium persulphate	10	6
Water	548	643
Non-ionic emulsifying agent	2	—

The bromoform and the triallyl phosphate are thoroughly mixed, and in the case of the 40% emulsion the emulsifying agent is added. The polyvinyl alcohol, as a 5% solution in water, is added with continuous stirring, followed by the sodium bicarbonate with all but 250 parts of water. The mixture is heated with stirring to 82–83°C. as rapidly as possible, and the potassium persulphate then added, followed by the remaining 250 parts of water. The temperature is kept at 80–85°C. with slow continuous stirring for 2 hr., and then the mixture is cooled rapidly. The pH of the final emulsion should be 7·2–7·5, and there should be no extensive creaming.

Fabric impregnated with this emulsion, dried, and heat-cured has good resistance to flaming and glowing, and these properties are fairly fast to washing. Fabric handle is generally affected, but this can be minimised by the use of a plasticiser such as 2–4% tetrabutyl thiodisuccinate. Fabric strength is not significantly affected.

9. COMBINED THPC–BAP FINISH

It has been claimed that a combination of the THPC finish and the BAP finish offers a number of advantages over either of the separate systems[26]. It is suggested that—

(*a*) Better flame-resistance is obtained as a result of synergism

(*b*) Loss in tear strength normally associated with a THPC finish is minimised

(*c*) Wash fastness is as good as that of a THPC finish

(*d*) There is more flexibility in processing, and one recipe will cater for a wide variety of fabrics.

There seems to be some difference of opinion on the validity of these claims, and there is little doubt that the combined finish would be more expensive than the THPC finish.

A typical recipe which has been recommended is as follows—

286 parts	THPC was dissolved in
375 parts	Water, and
54 parts	Triethanolamine added.
175 parts	Urea was dissolved in
375 parts	Water, and
173 parts	Trimethylolmelamine added. The two solutions were mixed, and
810 parts	33% BAP emulsion containing 12 parts Tetrabutyl thiodisuccinate added.

The mixture (claimed to be stable for 8 hr.) was applied to 8-oz. cotton twill to give a 70% wet pick-up. The fabric was dried at 100°C., baked at 140°C. for 5 min., then washed off, and after-softened. The weight add-on was 18–20%. Good anti-flame, anti-glow properties were claimed with satisfactory handle and strength, but sample finishes of this type which have been examined have shown signs of loss in flame-resistance with repeated alkaline scouring.

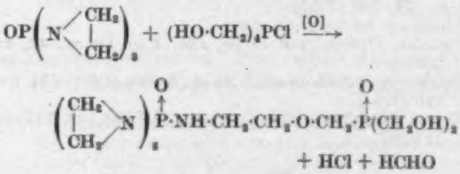
It is believed that some works development has been carried out in America using this combined finish, but whether any production has ensued is not known.

10. AZIRIDINYL COMPOUNDS

A recent development in the field of phosphorus flameproofing involves the use with THPC of trisaziridinylphosphine oxide or sulphide (APO or APS)[27], which are made by the reaction of ethylene-imine with phosphoryl or thiophosphoryl chloride in the presence of an acid acceptor such as tri-ethanolamine—

$$3\,HN\left\langle\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right. + POCl_3 \xrightarrow{-HCl} OP\left(N\left\langle\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right.\right)_3$$

APO and APS are low-melting-point compounds, readily soluble in water. They react with THPC at 100°C. and above to form thermosetting resins—



Further reaction of the aziridinyl rings with hydroxymethyl groups of THPC leads to the formation of a highly cross-linked polymer.

A solution containing equimolecular quantities of APO and THPC with triethanolamine ($\frac{1}{2}$ weight of THPC) is applied to fabric, which is then dried at 90°C., baked at 140°C. for 5 min., and finally washed off. It is claimed that good flame-resistance is obtained, fast to repeated washing in neutral detergent solution with as little as 7–8% solids add-on. At this concentration, very little reduction in strength occurs. For fastness to soap–soda scouring, 10% or more solids must be present, and under these conditions greater strength loss occurs. A 14% solids add-on corresponds to about 1·5% P and slightly less than 1·5% N.

As far as is known, this method has not progressed beyond the laboratory stage. Although only a relatively low solids add-on appears to be necessary, the cost of ethyleneimine would no doubt make the use of an APO system uneconomic at present.

Mechanism of the Flame- and Glow-proofing Action of Phosphorus Compounds

1. FLAME-RESISTANCE

When cellulose is degraded at high temperature it breaks down into a solid char, volatile liquids or tars, and gases [28]. The burning of cellulose depends on the relative amounts of these products formed. The ease of burning will be increased with ease of formation of flammable volatiles. Conversely, flame-resistance will be increased if the formation of solid char can be increased. Ideally, therefore, a flameproofing agent should promote the degradation of cellulose into carbon and water—

$$(C_6H_{10}O_5)_x \rightarrow 6xC + 5xH_2O$$

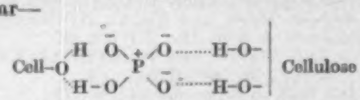
Effective flameproofing agents do increase the amount of char and decrease the amount of tar, and phosphorus-based finishes can give decomposition products corresponding to 80% of the theoretical dehydration of cellulose [29].

It has been reported [30] that the compositions of the tars from treated cellulose are very similar to those from untreated cellulose. This implies that the reduced flammability is due to a reduction in the quantity of flammable material formed rather than to a change in chemical composition of this material. With the reduction in formation of tar there is an increase in the amount of water formed. The dilution of the flammable vapours with this water may add to the effectiveness of the system.

The amount of dry gases evolved is approximately doubled by the addition of 5–10% of an effective flameproofer, but the same effect is produced by the use of sodium chloride [28]. In both cases the composition of the gases is similar to that from the untreated fabric, although the rate of formation is greater. It does seem, therefore, that flameproofing efficiency is not essentially a function of dry gas formation. It is interesting to note that sodium chloride is incapable of reducing tar formation below 30%, whereas effective flameproofers will reduce it to 5%.

Examination of the charred residues of cellulose treated with various organic phosphorus resins has revealed the presence of acids of phosphorus. It would appear that the effectiveness of phosphorus flameproofers lies in their ability to form acids capable of dehydrating cellulose at flaming temperatures. It is known that these acids can catalytically dehydrate alcohols and also esters, but in the latter case with the formation of acids instead of water. It has been suggested [9] that this indicates why cellulose acetate cannot be made flame-resistant with the agents that are effective on cellulose. Instead of water, acetic acid is formed, and this is inflammable in the gaseous state.

It has also been supposed [31] that phosphoric acid formed at flame temperature can form hydrogen bonds with the hydroxyl groups of the cellulose. If these bonds are sufficiently strong, they could prevent degradation of the cellulose into small volatile fractions, i.e. tars, and result in the formation of larger, less volatile fragments, i.e. char—



However, the weight of experimental evidence would appear to indicate that the predominant mechanism is one of acid dehydration, and that the effect of any bonding which might occur is secondary.

2. GLOW-RESISTANCE

The phenomenon of glowing is quite distinct from that of flaming, and different reactions are involved. That the prevention of afterglow depends on a different mechanism from that required to prevent flaming is shown by the fact that many effective flameproofing agents actually enhance afterglow. Phosphorus compounds are almost unique in their ability to prevent afterglow, and carbon chars containing phosphorus are remarkably resistant to prolonged heating. As little as 0·5% of some phosphorus compounds is effective in this respect, whereas as much as 10–12% may be necessary to prevent afterflaming. The efficiency of such small concentrations suggests a catalytic mechanism.

The oxidation of carbon to carbon dioxide is a much more exothermic reaction than the oxidation to carbon monoxide, and under normal conditions it is thought that this heat sustains glow—

$$C + \tfrac{1}{2}O_2 \rightarrow CO \quad \Delta H = -26\cdot4 \text{ kcal./mole}$$
$$C + O_2 \rightarrow CO_2 \quad \Delta H = -94\cdot4 \text{ kcal./mole}$$

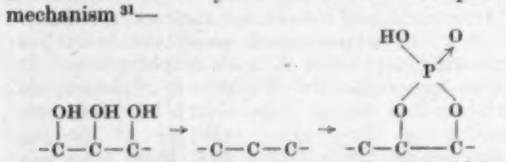
It is suggested that effective afterglow suppressors promote the oxidation to carbon monoxide, and under these conditions the heat evolved is insufficient to propagate glow. By controlled oxidation it has been shown [32] that the presence of

phosphorus in a carbon char does reduce the CO_2:CO ratio from approx. 4·5 to 0·5.

A possible mechanism is—

$$2H_3PO_4 + 5C \rightarrow 2P + 3H_2O + 5CO$$
$$4P + 5O_2 \rightarrow 2P_2O_5$$
$$P_2O_5 + 5C \rightarrow 2P + 5CO$$

Another theory is that the carbon char is deactivated by a surface adsorption mechanism [31]—



Certainly the phosphorus is very firmly held by the char, suggesting some form of actual combination. It has been established [33] that 95–97% of the total phosphorus present in the original fabric is retained in the char after combustion.

* * *

The author wishes to thank the Directors of Proban Ltd. for permission to publish this paper.

PROBAN LTD.
127 ROYAL EXCHANGE
MANCHESTER 2

(*MS. received 29th May 1958*)

References

1 D.S.I.R., *Second Report of the Fabrics Co-ordinating Research Committee* (London: H.M.S.O. 1930), p. 16.
2 Bowen, Majerus, Meals, and Kellett, *BP* 586,095.
3 Joseph Bancroft & Sons Co., *BP* 604,197.
4 Courtaulds Ltd., Morton, and Ward, *BP* 634,690.
5 Ward, F., J.S.D.C., **71**, 569 (1955).
6 Coppick and Hall, in Little, *op. cit.*[9], p. 179.
7 Davis, Findlay, and Rogers, *J. Textile Inst.*, **40**, T 839 (1949).
8 Jurgens, Reid, and Guthrie, *Text. Research J.*, **18**, 42 (1948).
9 Little, *Flameproofing Textile Fabrics* (New York: Reinhold Publishing Corpn. 1947), p. 190.
10 Neussle, Ford, Hall, and Lippert, *Text. Research J.*, **26**, 32 (1956).
11 American Cyanamid Co., *BP* 638,434.
12 Thomas and Kosolapoff, *USP* 2,401,440.
13 Reeves, McMillan, and Guthrie, *Text. Research J.*, **23**, 527 (1953).
14 Nielsen, *ibid.*, **27**, 603 (1957).
15 Monsanto, Malowan, and Hurley, *BP* 683,572, 700,822.
16 Pollack, *USP* 2,418,525.
17 Pollack and Fassal, *USP* 2,464,342.
18 Pingree, Ackerman, and Sun Chemical Corpn., *USP* 2,488,034.
19 Reeves and Guthrie, *Agriculture & Industrial Chemistry* (2nd Nov. 1953), p. 364.
20 Hoffmann, *J. Amer. Chem. Soc.*, **43**, 1684 (1921).
21 Reeves and Guthrie, *Dyer*, **111**, 567 (1954).
22 Idem, *Ind. Eng. Chem.*, **48**, 64 (1956).
23 Albright & Wilson Ltd., *BP* 740,269; Bradford Dyers' Assocn. Ltd. and Albright & Wilson Ltd., *BP* 761,985.
24 Glenn L. Martin Co., *BP* 700,292, 700,604.
25 Frick, Weaver, and Reid, *Text. Research J.*, **25**, 100 (1955).
26 Reid, Frick, and Arenceaux, *Text. Research J.*, **26**, 141 (1956).
27 Reeves, Drake, Chance, and Guthrie, *Text. Research J.*, **27**, 260 (1957).
28 Little, *Amer. Dyestuff Rep.*, **36**, 136 (1947).
29 Schuyten, Weaver, and Reid, *Ind. Eng. Chem.*, **47**, 1433 (1955).
30 Parks, Antoni, Petrarca, and Pitochelli, *Text. Research J.*, **25**, 789 (1955).
31 Little, *op. cit.*[9], pp. 80 *et seq.*
32 Coppick, Church, and Little, *Ind. Eng. Chem.*, **42**, 415 (1950).
33 Stansbury and Hoffpauir, *Amer. Dyestuff Rep.*, **44**, 645, 676 (1955).
34 Tootal Broadhurst Lee Co. Ltd., *BP* 704,143, 713,001, 713,002.

Discussion

(MANCHESTER)

Mr. G. COE: Does steam curing as patented by the Tootal Broadhurst Lee Co. Ltd.[34] help in minimising the loss in strength which results from the application of the THPC process followed by dry heat curing?

Mr. PERFECT: Steam curing does not appear to be as satisfactory as dry heat curing in the production of a THPC finish. The fastness of the finish to washing is superior when dry heat curing is used. Presumably this implies that steam curing inhibits polymerisation to some extent.

Mr. J. V. BUTCHER: In the application of Proban-type finishes is it necessary to follow drying and baking of the resin with an oxidation treatment, and if so why?

Mr. PERFECT: Yes, an oxidising scour after curing is an integral part of the Proban finish.

The THPC-based polymer formed on the fabric during curing contains some $\geq$P→. This can act as a reducing agent and, particularly on exposure to light, cause reduction of dyes on the fabric. Oxidation forms $\geq$P→O and eliminates this trouble. Also, vat dyes, during the padding, drying, and curing stages, are reduced to leuco compounds, and an oxidising scour is necessary to restore the original colours. As far as white goods are concerned, an oxidation treatment minimises any yellowing which is produced by the finish.

Mr. D. BLACKBURN: In view of the speaker's remarks regarding the release of flammable acetic acid vapour from cellulose acetate during burning, does this mean that the Proban finish as applied to cellulose acetate, or cellulose acetate–cellulose blends, will render them more flammable than the untreated material?

Mr. PERFECT: The Proban finish will certainly not render cellulose acetate rayon fabrics flame-resistant. Whether it makes them more flammable is not known.

Cellulose acetate rayon–cotton (or –viscose rayon) blended fabrics may be satisfactorily treated with the Proban finish providing that the acetate rayon content is less than 15% of the total fabric. Presumably this effect is achieved simply because the non-flammability of the cellulosic portion smothers any tendency for the acetate to burn.

Water-repellent Finishes— Modern Use of Silicones

G. W. MADARAS

One-day Symposium on "New Information on Finishing Processes" held by the Manchester Section at the Manchester College of Science and Technology on 21st March 1958, Mr. J. W. Reidy in the chair

Recent developments in the application of silicones to textiles are discussed. Advantages as well as shortcomings of treatments from organic-solvent solutions and aqueous emulsions are outlined. The importance to the industry of low-temperature-curing silicone compositions is stressed, and the function of organo-metallic titanium compounds in bringing about low-temperature catalysis is explained.

In the water-repellent field the quest for novel finishes has produced a variety of chemicals and processes, amongst which silicones are the most recent arrivals. Only seven years have elapsed since silicones were first used on a commercial scale in the finishing industry of this country, so it is hardly surprising that they have not yet found the general acceptance they deserve.

The synthesis in 1901 of tetra-substituted asymmetric silicon compounds by Kipping and his co-workers at University College, Nottingham, created a sustained interest in organo-silicon chemistry, and for some 40 years Kipping's school of chemistry was engaged in extending this work to see whether a whole system of chemistry could be based on this element in the way organic chemistry is based on carbon. These researches provided a firm foundation for much, if not all, of the subsequent developments. In their work, Kipping and his co-workers were frequently confronted— and confounded— by sticky, oily, rubbery, and generally intractable materials, which they recognised as polymeric, containing Si–O bonds, but were unable to separate or identify. In the Bakerian Lecture to the Royal Society in 1937, Kipping stated that: "... the prospect of any immediate and important advance in this section of organic chemistry does not seem to be very hopeful". This frequently quoted prognostication has turned out to be wrong, but had it not been for the Second World War, the commercial and industrial exploitation of Kipping's findings might have been much slower. Be that as it may, the demand created for new materials working for long periods under extremes of temperature, pressure, etc. proved a great stimulus to the study of the chemistry of high polymers and caused a re-opening of the chapter on organo-silicon polymers which had so frequently complicated life for the workers at Nottingham.

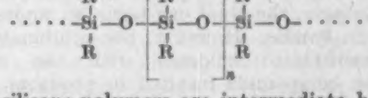
Amongst the compounds investigated were those obtained by the hydrolysis of dialkyldichlorosilanes R_2SiCl_2 and called "silicones" by Kipping by analogy with the ketones—

$$R_2SiCl_2 \longrightarrow R_2Si(OH)_2 \longrightarrow (R_2SiO)_n$$

The intermediate dihydroxy compound might have been expected to behave similarly to its carbon analogue, losing water to form an >Si:O bond. Although water is in fact lost readily, it is split off intermolecularly to form polymeric materials having an –Si–O–Si–O– or *polysiloxane* structure, and generically referred to as *silicones*. This work was primarily carried out in the U.S.A. by the General Electric Company and the Dow Corning Corporation, and by 1949 commercial products made from silicones had firmly established themselves in the U.S.A., and were beginning to be looked upon less as a chemical curiosity over here. Initial outlets were as insulating materials in the electrical industry, but their usefulness as lubricants and greases won them admission into many branches of engineering, whilst their water-repellent property is now utilised by a variety of industries, e.g. the building, textile, and leather industries.

STRUCTURE AND NATURE OF SILICONES

A typical polymeric silicone or siloxane built up of alternating Si–O–Si–O atoms has an inorganic backbone not unlike that of silica, the organic radicals R satisfying the remaining valences of the silicon being generally methyl or phenyl—



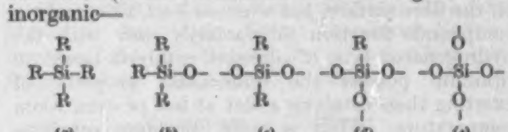
These silicone polymers are intermediate between inorganic and organic, a kind of hybrid. This is further shown by reference to three siloxane units — (*b*), (*c*), and (*d*)— which form the basic bricks of practically all silicone polymers. Depending on the number of residues R attached to the silicon atom, these units serve to—

Stop the growing chain: *chain-stopper* (*b*)

Build the growing chain: *chain-former* (*c*)

Branch and cross-link the growing chain: *cross-linker* (*d*).

These three units fit into the series which is entirely organo-metallic at one end (*a*), and entirely inorganic at the other end (*e*), which explains their intermediate character between organic and inorganic—

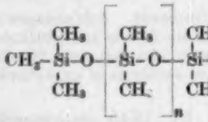


(*a*) Organo-metallic; (*b*) Mono-functional Chain-stopper; (*c*) Di-functional Chain-former; (*d*) Tri-functional Cross-linker; (*e*) Purely Inorganic Silica SiO_2

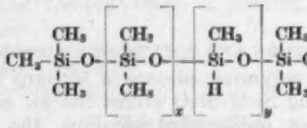
The silicones which result from appropriate combination of these units or bricks are fluids, elastomers, or resins, and some of their common features are— (i) resistance to heat (extremes of temperature generally), (ii) resistance to sunlight, (iii) chemical inertia.

WATER REPELLENCY

Application of a silicone fluid or resin to any surface renders the latter powerfully water-repellent. Linear dimethylpolysiloxane fluids which exhibit this strongly water-repellent effect are the prototype of the silicones which are of most interest to the textile industry—



The application of these compounds alone to textiles would lead to undesirable results, as a temperature of 200–250°C. maintained for several hours is required to bring about a water-repellent effect. To overcome this difficulty, silicone manufacturers have altered the structure of the fully methylated product by introducing a proportion of reactive groups, e.g. hydrogen atoms, resulting in products of the type—



Methyl Hydrogen Silicones

The use of methyl hydrogen silicones by themselves, although conferring good water-repellency at temperatures of about 150°C., suffered from other disadvantages, the chief one being an undesirable change in handle. However, the combination of fully methylated silicones with the methyl hydrogen compounds resulted in products which were particularly suitable for textile application, and are still the most widely employed in our industry.

CATALYSTS

Even these "textile silicones" are not by themselves entirely suitable as water repellents, and to obtain satisfactory polymerisation or hardening of the silicone fluid on the fibre surface, the use of catalysts or *hardening agents* is required. A number of metal compounds will act as catalysts, *inter alia* the fatty-acid salts of lead, zinc, and tin, as well as the alkyl esters of orthotitanic and orthozirconic acids, e.g. butyl titanate. These compounds act by reducing both the temperature and the time required for the silicone to harden or polymerise on the fibre surface, but whereas lead, zinc, and tin compounds function satisfactorily only with the hydrogenated type of silicones, catalysts based on titanium possess the remarkable property of exerting their catalytic effect at low or even room temperature. What is more, titanium catalysts are effective not only with the methyl hydrogen type of silicones, but bring about entirely satisfactory union between the fibre and the less reactive silicones and even the non-reactive types. (Less reactive silicones are generally understood to be those which contain no Si–H groups, but which may contain other polymerisable groups such as Si–OH or Si–O·Alk, whilst the non-reactive types contain $Si–CH_3$ or similar residues only.)

TABLE I

Effect of Two Metal Catalysts on the Water Repellency obtainable from Reactive and Non-reactive Silicones

(Application from organic solvent on cotton gaberdine by padding, drying, and baking at 160°C. for 3 min.)

Treatment	Bundesmann Test Absorption (%)	Penetration (c.c.)
REACTIVE SILICONE		
2% Silicone	46	53
0·125% Butyl titanate	64	60
0·125% Zinc octoate (octanoate) ...	60	57
2% Silicone + 0·125% butyl titanate	25	1
2% Silicone + 0·125% zinc octoate	31	0
NON-REACTIVE SILICONE		
2% Silicone	75	134
1% Butyl titanate	42	25
1% Zinc octoate	62	35
2% Silicone + 1% butyl titanate	26	2
2% Silicone + 1% zinc octoate	55	44

Table I shows that synergism exists between metal catalysts and reactive silicones; with non-reactive silicones the zinc catalyst is ineffective, but the titanium compound is effective, and synergism still applies. These two examples provide the key to the unusual behaviour of the titanium catalyst, viz. to its dual function. In the first case butyl titanate functions not unlike the zinc compound by causing gelation or hardening of the silicone fluid, thereby inducing further polymerisation as well as cross-linking. It is generally considered that the following type of reaction takes place—

$$\mathrm{R{-}Si{-}H \longrightarrow R{-}Si{-}OH}$$

$$\mathrm{R{-}Si{-}OH + HO{-}Si{-}R \longrightarrow R{-}Si{-}O{-}Si{-}R + H_2O}$$

possibly with the incorporation of the metal—

$$\mathrm{R{-}Si{-}O{-}Ti{-}O{-}Si{-}R}$$

However, in the second case there are no reactive groups available in the silicone, and the titanium compound must therefore act by some other mechanism. The ease with which butyl titanate and other titanium compounds co-ordinate may explain the second mechanism, since probably the titanium compound links up with the fibre surface on the one hand and with the silicone chain on the other, thereby anchoring the silicone to the fabric. It is probable that this second mechanism also plays a part in the hardening of reactive silicones (i.e. those containing Si–H bonds) with butyl titanate; this explains why use of titanium compounds frequently leads to better fastness results than those obtained with other metals.

METHODS OF APPLYING SILICONES

The application of silicones to textiles falls broadly into two groups—

(1) Application from organic-solvent solutions

(2) Application from aqueous emulsions.

Both methods can be subdivided into—

(a) Treatments requiring curing or polymerisation at elevated temperature

(b) Treatments carried out at ordinary drying or even at room temperature.

SOLVENT TREATMENT WITH CURING AT ELEVATED TEMPERATURE

It is generally agreed that application of a silicone from an organic-solvent solution gives better initial water repellency coupled with better fastness properties than application of the same silicone from an aqueous medium. To confirm this the same silicone components were applied from solvent solution and aqueous emulsion to the same range of fabrics. The silicone take-up was kept the same, and in both experiments polymerisation was effected at elevated temperature (Table II).

TABLE II

Comparison of a 2% Silicone Treatment applied from Organic Solvent and from Aqueous Emulsion

Fabric	From Solvent		From Emulsion	
	Bundesmann Test			
	(%)	(c.c.)	(%)	(c.c.)
Cellulose acetate poult	11	1	25	4
Cotton gaberdine ...	13	1	31	2
Wool gaberdine ...	13	2	37	2

The advantages of the solvent treatment are—

(1) Applicability to all fibres without exception

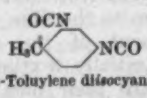
(2) No swelling of the fibres, and hence no undesirable dimensional changes

(3) No need for emulsifying agents, and hence no risk of impairing the proof.

*ISO*CYANATE PRETREATMENT

A very recent development which has given satisfactory results consists in combining an *iso*cyanate treatment with the silicone process. This combined treatment is usually applied in two steps, but it is possible, at least on a laboratory scale, to apply it in one stage.

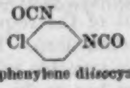
Di*iso*cyanates, which have proved particularly effective, are—



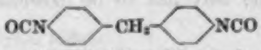
m-Toluylene di*iso*cyanate

$OCN \cdot [CH_2]_6 \cdot NCO$

Hexamethylene di*iso*cyanate



Chlorophenylene di*iso*cyanate



Diphenylmethane di*iso*cyanate

Treatment of the yarn or fabric in an organic-solvent solution of one of these di*iso*cyanates is followed by drying and curing. Next the material is treated with the desired silicone and catalyst dissolved in an organic solvent. This is followed by drying and baking. Table III shows how effective this pretreatment is on a cotton gaberdine.

TABLE III

Effect of Pretreatment with *m*-Toluylene Di*iso*cyanate on the Wash Fastness of a Silicone Treatment on a Cotton Gaberdine

(2% Reactive silicone + 0·125% butyl titanate— cf. Table I. Bundesmann test absorption (%) and penetration (c.c.))

No. of Washes*	Without		With	
	Pretreatment			
	(%)	(c.c.)	(%)	(c.c.)
0	25	1	12	1
1	45	23	29	1
3	48	34	28	1
5	55	37	31	1

* 2 g. Soap per litre (50 : 1 liquor ratio) at 60°c. for 90 min.

SOLVENT TREATMENT AT REDUCED OR ROOM TEMPERATURE

Although it is probably true that mills which would be prepared to undertake working with organic solvents would also have facilities for high-temperature curing, a closer look at the problem will indicate a variety of applications of silicones to textiles and other substrates where recourse to a high-temperature treatment is undesirable if not impossible.

Silicone–Titanate Compositions

By selecting the right types of silicones (not containing Si–H bonds) it has been found possible to prepare mixtures in a suitable (water-immiscible) organic solvent of silicones and alkyl titanates. These are perfectly stable to storage as long as moisture is excluded, and merely require diluting with any suitable organic solvent, e.g. white spirit. These diluted silicone–titanate compositions have a working life of at least 12 hr., frequently much longer. They can be applied to textiles and other materials, especially leather and footwear, by a variety of methods, e.g. padding, brushing, dipping, spraying, etc. The treated materials, be they tarpaulins, garments, or piece goods, then merely require drying, which can be done in any conventional way, using any existing plant; or if so desired the material can be left to dry in air. After drying, the water repellency continues to develop, and optimum results are obtained after 24–48 hr. These compositions are manufactured in this country by Midland Silicones Ltd., in France by Société des Usines Chimiques Rhône-Poulenc, and in Belgium by Union Chimique Belge, and are freely available here.

Mechanism of Catalysis

Only organo-titanium compounds appear to show this remarkable property of functioning as good catalysts for silicones at room temperatures. We can assume that a hydrolysed form of the titanium catalyst attaches itself to the fibre surface by secondary valency forces, and the silicone chains are then anchored to the titanium-studded fibre surface via their oxygen atoms. The silicone chains are probably elongated so that the Si–O backbone

is oriented towards the fibre, and the water-repellent methyl groups point away from it, giving an umbrella-like protection. It is the interaction between the titanium and the silicone chains which is responsible for the excellent water-repellent effect, and that this is not merely due to the alkyl titanate functioning as a water-repellent *per se* is demonstrated by the results in Table IV.

TABLE IV

Synergistic Effect between Silicones and Alkyl Titanates

(Application from organic solvent on cotton gaberdine by padding, drying, and curing in air for 48 hr.)

Treatment	Bundesmann (%)	Bundesmann (c.c.)
2% Silicone	49	61
2% Butyl titanate	45	26
2% Commercial product* ...	28	1

Commercial product (50% solids) containing silicones and alkyl titanates.

The synergistic effect between silicone and butyl titanate is therefore convincingly demonstrated, although this view has been the subject of some contention in the past. Another charge levelled occasionally at these air-curing silicone–titanate compositions is that their initial water-repellency, and particularly their resistance to alkaline washing and dry-cleaning, is inferior to the proof obtainable from the so called fully cured silicones, i.e. those containing Si–H groups and polymerised at a high temperature. Whilst it would be incorrect to argue that cold-curing silicone–titanate compositions and highly reactive textile silicones cured at, say, 150°C. give identical results, the differences are generally slight, and are frequently marginal (cf. Table V).

TABLE V

Comparison between a Baking and an Air-curing Silicone Treatment

Treatment*	Treated (%)	Treated (c.c.)	Washed (%)	Washed (c.c.)	Solvent-rinsed (%)	Solvent-rinsed (c.c.)
	Bundesmann					
Nylon						
A ...	9	70	8	74	11	80
B ...	6	94	9	72	20	145
Secondary Cellulose Acetate						
A ...	11	1	13	1	20	1
B ...	14	2	18	2	24	2
Cotton						
A ...	25	1	33	7	34	1
B ...	36	1	41	17	45	13
Wool						
A ...	13	2	24	2	17	2
B ...	18	1	38	1	46	4

* A = 2% Silicone + 0·125% butyl titanate cured at elevated temperature.
B = 2% Commercial product (see Table IV), air-cured for 48 hr.

Uses

Amongst the outlets for cold-curing silicone–titanate compositions the following come to mind—

(i) Industrial fabrics, e.g. canvases, sail-cloths, felts
(ii) Delicate fabrics and also those made from heat-sensitive fibres
(iii) Coated fabrics; e.g. resin-coated nylon rainwear can be made non-tacky and given better pearling properties
(iv) Made-up articles, e.g. tents, garments, furnishings
(v) Articles which have been dry-cleaned can be easily reproofed.

Advantages

Before leaving this air-curing system we may briefly recapitulate some of its advantages—

(1) Excellent water repellency
(2) Unchanged vapour-transmission properties of treated fabrics
(3) Improved flexibility, drape, and handle of treated fabrics
(4) These compositions are compatible with a large variety of other finishing agents, e.g. rotproofing agents, antibacterial finishes, stiffening agents, mothproofing agents
(5) Repair of treated fabrics or articles, e.g. tarpaulins, tents, marine canvases, can be carried out under field conditions
(6) Anti-stick properties
(7) No investment in expensive baking equipment.

EMULSION TREATMENTS

Since organic-solvent treatments are not favoured by the textile industry, the silicone manufacturers have met its needs by supplying their products in the form of aqueous emulsions. In the preparation of such emulsions it must be borne in mind that emulsions of textile silicones, i.e. those containing reactive silicones, have a limited stability and show a tendency to evolve hydrogen; such emulsions are particularly unstable to alkaline water. Another difficulty is the choice of a suitable emulsifying agent, as most of them, being surface-active, exert a wetting action when introduced on to the fibre surface, with the resultant impairment of the optimum water-repellent effect. Initially textile processers were expected to prepare their own emulsions; but nowadays reasonably stable emulsions are available, and when they are supplied to the finisher, the silicone manufacturers provide him with the appropriate amount of the required catalyst (also frequently as an emulsion). The use of crease-resist resins is often possible with such emulsions, although some care has to be exercised to avoid fishy odours.

Cold-curing Emulsion for Protein Fibres

Whilst the marketing of cold-curing silicone–solvent compositions has been a big step in the right direction, attempts at producing silicone emulsions which do not require baking have

received much attention. Recently one large firm of silicone producers has developed a silicone emulsion which shows two very desirable features. Firstly, the emulsion is substantive to wool and other protein fibres: in other words, it exhausts on to such yarns or fabrics. Secondly, no high-temperature curing is required, the treated material merely requiring drying in any standard fashion. This development is of considerable importance to the wool industry, since it makes it possible for the finest and most delicate yarns and fabrics, be they knitted or woven, to be treated with silicones on any existing plant; e.g. a dolly or a winch machine is ideally suited for wool cloths.

The silicone emulsion is mixed with the appropriate amount of catalyst solution, which is again an organic derivative of titanium, and the catalysed silicone emulsion is let down with water and added to the dolly or vessel. The goods to be treated have previously been wetted out, and the bath has been brought to pH 4–6. The recommended liquor ratio is 30:1, but it can be varied over wide limits, good results having been obtained at 20:1 and 40:1. On adding the diluted catalysed silicone emulsion to the machine, the bath looks milky, but the milkiness begins to clear within 5–10 min. and the liquor is completely clear after 15–25 min. It is recommended to continue for a further 10 min. so that complete penetration can take place. When the treatment has been completed, after 25–35 min., the goods are hydro-extracted and then dried in any conventional way. It is important to realise that the water repellency continues to develop during storage after drying, and the maximum effect is obtained after 10–14 days.

This treatment, the latest development in the field of combined water- and stain-repellency, has been available for only about a year. It is applicable primarily to wool and to yarns and fabrics containing a preponderance of wool (about 80%). However, very good results have been obtained also on some wool–Terylene unions, wool–Acrilan blends, and wool–viscose rayon staple mixture fabrics.

It is interesting to compare the water repellency obtained in this way with those resulting from a conventional organic-solvent treatment on the one hand and from an aqueous emulsion treatment on the other. In both these latter treatments the sequence of operations was padding, drying at 80°C., and baking at 150°C. The new substantive silicone emulsion was applied to the fabric by the exhaust treatment described above. Maximum water repellency was allowed to develop at room temperature. In these experiments a typical all-wool gaberdine (14 oz.) was used, and 2% silicone solids were deposited (Table VI).

TABLE VI

Comparison of Three Silicone Treatments on an All-wool Gaberdine
(Bundesmann Test Results)

	Substantive Emulsion*		Commercial Products (Solvent)†		(Emulsion)†	
	(%)	(c.c.)	(%)	(c.c.)	(%)	(c.c.)
As treated	42	2	12	2	35	2
After 14 days	13	1	12	2	35	2
Solvent-rinsed	18	2	18	2	48	2

* Air-cured.

† Both commercial silicone products were non-substantive, and were cured at elevated temperature.

Table VI shows that the results obtained with the substantive silicone emulsion may approximate to, if not equal, the results obtainable from a solvent treatment. The conventional emulsion treatment is a poor third. To summarise, it can be said that this new substantive silicone emulsion can give water and stain repellencies which are almost equal to those obtainable from a solvent treatment. This development has marked an enormous advance in the quest for a cold-curing silicone emulsion; the mode of application as well as the absence of any high temperatures has made it possible to apply silicones to a whole host of fabrics, where previously a conventional silicone treatment had been considered impracticable.

Cold-curing Emulsion for other Fibres

There is a demand for a cold-curing silicone emulsion which is applicable to fibres other than wool, particularly to the cellulosic and synthetic fibres, and considerable progress has been made toward finding a solution to this problem. Although no actual commercial process is as yet in existence, bulk-scale trials have been carried out with satisfactory results. Again the choice has fallen on organic derivatives of titanium to provide the catalyst which would effectively key the silicone chains to the fibre surface at low or even room temperature. Table VII shows a strict comparison between our new air-curing silicone emulsion and a commercial one which requires polymerisation at elevated temperature.

TABLE VII

Comparison of Experimental Air-curing Silicone Emulsion with a Commercial Product requiring a High-temperature Cure
(2% Silicone Solids)

Fabrics	Experimental Product* Bundesmann (%)	(c.c.)	Spray Test	Commercial Product† Bundesmann (%)	(c.c.)	Spray Test
Nylon taffeta	10	51	100	10	46	100
Cellulose acetate poult	20	1	90	23	1	90
Cotton gaberdine	26	1	100	30	1	100
Wool gaberdine	11	1	100	11	1	100
Union gaberdine	29	1	100	34	1	100

* New low-temperature-drying silicone emulsion with titanium catalysts; dried at 80°C., then air-cured for 48 hr.

† Commercial product, comprising a commercial silicone emulsion with appropriate catalyst; dried as above, then cured at elevated temperature.

CORRELATION OF TEST RESULTS

Frequently one is asked whether it is possible to correlate results obtained by different tests. The answer to this depends on a variety of factors, particularly which tests are to be compared, on what fabrics, etc. It is often convenient to use the Standard Spray Test as a rough sorting test, particularly for investigations which entail the evaluation of the effects of a large number of variables and which therefore produce an abundance of patterns, but it is advisable to check by a more rigorous procedure as soon as possible. This is speaking from bitter experience, since in the course of the development of our cold-curing catalyst system we thought at one stage that we had achieved success. A range of fabrics treated by the new method all gave values of 100 by the Standard Spray Test, but a rude awakening came weeks later, when some more of the same fabrics were submitted to the Bundesmann test, and high absorptions (cellulose acetate 47%, cotton 81%) and even higher penetrations (14 and 47 c.c.) were returned. The differences were so astounding that we first looked for an error in testing, but to no avail, for the same results were repeated. Finally, there was nothing left but to watch the patterns being rained on during the Bundesmann test, when we realised what was happening. For the first 90 sec. all was well, and then suddenly the proof broke down; indeed, the suddenness was quite uncanny. Thus, according to the Standard Spray Test the proof was perfect (the total time the fabric was sprayed in the course of this test was approx. 30 sec.), but according to the more severe Bundesmann procedure, the proof was a wash-out in more than one sense of the term.

CONCLUSIONS

If strict comparisons are made, the initial water repellency is almost always found to be superior with silicone-treated fabrics than with other proofing methods, and this relation continues throughout the life of the fabric.

Of considerable interest is the property conferred by silicone treatment on yarns or fabrics of resisting staining if milk, ink, or alcoholic drinks are spilled on them.

The porosity of the treated fabric is unchanged, i.e. water vapour can diffuse freely (although the fabric resists the passage of liquid water). Hence the ability of the fabric to "breathe" is unaffected. Use of cold-curing silicone–titanate compositions, the application of which is quite simple, makes it possible to effect running repairs to tarpaulins, tents, etc. whilst in use. To obtain the desired water-repellent effect only 1–2·5% silicone solids are required, so that there is no loading of the material with foreign matter. This is why the handle of the silicone-treated fabric is either unchanged or more frequently softer than before treatment. Should that be undesirable, it is possible, of course, to modify handle as desired.

In conclusion, it is appropriate to reiterate that, without the fundamental work of Kipping and his school, the subsequent technological advances, which have resulted from a resourceful application of silicones to textiles, would not have been possible.

SILICONE PROCESSES LTD.
39 WELL STREET
BRADFORD 1
YORKSHIRE

(*MS. received 8th May 1958*)

Discussion

Dr. J. A. C. WATT: We can confirm at Nobels' Research Department the lecturer's experience with regard to water-repellency assessments by the Spray Rating and the Bundesmann tests: with thick cloths it is possible that the surfaces may be treated to a greater extent than the interior of the cloth, giving a sandwich effect. Such a treatment can yield a spray rating of 100, since this test employs only a light spray, but in the Bundesmann test the water drops have sufficiently high energy to penetrate the surface and wet the interior of the cloth. The effect is particularly noticeable in some samples of wool–Terylene blends in which wetting agent, used for prior processing, has been removed only from the surfaces of the cloth but not from the interior.

Dr. MADARAS: Both tests have their uses, but care has to be exercised in interpreting the results of the Spray Test. The spurious good water repellency occasionally given by a Spray Test may indeed be due to a sandwich effect with thick fabrics, but since our observations relate also to fabrics such as cellulose acetate taffetas and poults as well as cotton gaberdines, I think that this anomaly is more likely to be due to the relatively mild conditions employed in the test, which do not sufficiently tax the ability of the fabric to repel water.

Dr. WATT: With regard to the comparison of solvent and emulsion processes, while we agree with Dr. Madaras's views concerning wool, our experience with cotton has shown the opposite effect. Cotton treated from emulsion becomes slightly more repellent than that treated with similar materials from solvent. For example, with a 2% pick-up, emulsion treatment followed by baking at 130°C. for 5 min. gives a Bundesmann absorption of 15–20% on cotton gaberdine; with a similar solvent process the values are 20–30%. The difference in behaviour between cotton and wool suggests that the type of emulsifying agent is important, and an indication of the emulsifying agents employed by the lecturer would be of interest.

Dr. MADARAS: I am unable to agree with your observations that the results of a solvent treatment on cotton are inferior to those of an emulsion treatment. Although it is generally observed that the application of silicones to cotton and other cellulosic fibres gives less satisfactory results than on protein or synthetic fibres, the trend remains unaltered. In fact, I find it difficult to comprehend why an emulsion treatment should give better results than the same treatment from an organic solvent. With careful choice of emulsifying agents it is feasible that the emulsion treatment might come up to the results of the solvent treatment, but in my view it can hardly better it. In

Table VIII are given typical results obtained with two British manufacturers' silicone products recommended for the treatment of cotton. Both solvent and emulsion products were applied with the appropriate catalysts, and the treatments were carried out in accordance with the instructions given by the manufacturers.

TABLE VIII

Treatments on Cotton Gaberdine

Treatment	Manufacturer I		Manufacturer II	
	(%)	(c.c.)	(%)	(c.c.)
2% Silicone from organic solvent	13	0	14	0
2% Silicone from aqueous emulsion	26	2	29	2

In reply to your last point I agree that the type of emulsifying agent used is most important, and in the development of a low-temperature-curing silicone–catalyst system we prefer a cationic emulsifying agent of the quaternary ammonium type.

Dr. A. R. URQUHART: Dr. Madaras's beautiful demonstrations indicate that virtually no water would be retained by a showerproof made from his treated fabrics. Inevitably, however, much of the water that would be repelled by the finish would be retained by the trousers below the coat. For such usage, therefore, would it not be better to use a fabric that shows minimum penetration coupled with *maximum* absorption in the Bundesmann test?

Dr. MADARAS: Up to a point it might be desirable for a showerproof fabric to behave as Dr. Urquhart suggests; indeed, some woollen manufacturers go a long way to meet these recommendations. However, the course advocated, viz. the combination of maximum absorption with minimum penetration, raises more problems than it solves, and taken to its logical conclusion would result in treated fabrics possessing all the characteristics of a sponge. Thus, on exposure to heavy and prolonged rain, such fabrics would readily absorb 2 or 3 times their own weight of water, this weight increase alone adding much to the wearer's discomfort. Further, subsequent drying would be a tedious task. Even if such extreme measures were not contemplated, it is still difficult to define "maximum absorption" in terms of actual usage. Would, in the opinion of the questioner, this maximum be reached, say, after 15 min. or after 45 min. exposure to heavy rain? In view of the obvious difficulties inherent in adopting a satisfactory standard based on maximum absorption and minimum penetration, might it not be more expedient to have the trousers silicone-proofed as well?

Mr. J. GREENWOOD: Will the lecturer enlarge on the stain-resisting qualities of silicone finishes?

Dr. MADARAS: Silicone-treated fabrics show outstanding resistance to all water-borne stains, such as ink, tea, coffee, beer, wine, cocktails, fruit juices, etc. Fabrics accidentally contaminated with any of the above do not become stained, since the offending liquid forms droplets which pearl off or simply rest on the fabric surface without penetrating it. Generally, these droplets will shake off quite readily; should any residual staining be apparent, this can be removed by sponging with a wet cloth. The importance of conferring stain repellency on their fabrics and garments has been recognised by clothing and knitwear manufacturers, and an increasing proportion of silicone treatment is nowadays carried out with this object in view.

A silicone finish does not, however, confer resistance to oily or greasy contamination, although fabrics so contaminated can be readily dry-cleaned without materially affecting the water- and stain-repellent properties of the silicone proof.

Mr. H. T. FERGUSSON: How does a silicone proof on cotton twill affect tensile strength, abrasion, tear strength, and stitchability?

Dr. MADARAS: The application of most chemical finishes to cotton twill brings about a change in physical properties, and silicones provide no exception. Nevertheless, undesirable changes are a minimum, while considerable improvements also occur. Thus, of the four properties mentioned, it can be said that, in general—

(i) The tensile strength is very slightly reduced, but the loss rarely exceeds 10%.

(ii) The tear strength is increased, and improvements of up to 30% have been observed.

(iii) The abrasion resistance is somewhat improved, although it may be misleading to quote actual figures, as much depends on the type of abrasion measured, e.g. flat or folded abrasion, on the apparatus used, and on the abrasive fabric employed. There is evidence in the literature[1,2] that improvements amounting to a twofold increase in abrasion resistance have been observed.

(iv) Finally, better stitchability results owing to the fact that silicones, having a lubricating action, reduce both needle and thread friction. Less overheating of the needle takes place, and the size of the needle holes is reduced, resulting in fewer tears.

Dr. C. J. W. HOOPER: In the demonstration experiment the water appears to be dripping through the bag at its surface, not through the bottom of the bag as would be expected. Why is this?

Dr. MADARAS*: The reason for the untreated control initially refusing to leak and later behaving anomalously is now apparent. A few days before the lecture the untreated canvas was submitted to the standard bag test, and water leaked through the bottom of the bag, as expected, in a short while. We did not realise, however, that, on drying, this fabric shows considerable shrinkage, which results in a reduction of the interstices (porosity) of the fabric. On renewed wetting, as shown by the demonstration, the fabric resisted the passage of water for a considerable time (it did ultimately leak again). The reason for the water dripping through at the surface of the liquid is simply that the upper portion of the fabric had not been wetted in the laboratory test, and hence no dimensional changes had taken place there.

* Communicated.

References

[1] Cook, A. A., *Amer. Dyestuff Rep.*, **45**, P 771 (1956).

[2] Weltzien, G., and Hauschild, G., *Melliand Textilber.*, **37**, 695 (1956).

The Finishing of Cellulose Triacetate Fabrics, with particular reference to Setting, Embossing, and Pleating

S. N. BRADSHAW and A. S. CLULEY

Meetings of the Scottish Section held at the St. Enoch Hotel, Glasgow, on 18th March 1958, Mr. W. G. B. Grant in the chair; and at the One-day Symposium on "New Information on Finishing Processes" held by the Manchester Section at the Manchester College of Science and Technology on 21st March 1958, Mr. J. W. Reidy in the chair

The purpose of this paper is to review and summarise knowledge of thermal finishing of fabrics containing Tricel, and an attempt has been made to define the reasons for the different methods in use and to specify the sequence of operations in processing.

SOME THEORETICAL ASPECTS

As a general rule, the thermoplastic fibres have a low water imbibition, and consequently exhibit little swelling in water. Cellulose triacetate fibres have a normal water imbibition of 17%, which can be reduced to 10–12% by suitable heat treatment. For this reason it is important that, if the maximum development of the desired properties (e.g. wet elastic recovery) is to be obtained, fabrics containing a substantial proportion of Tricel should be given heat treatment at some stage during dyeing and finishing.

The importance of heat setting was recognised as early as 1950–1951, when much of the initial work on the setting of cellulose triacetate fibres was carried out. The recognition of the profound effect of heat setting upon the properties of the fibre necessitated a detailed study to establish the test conditions required. As with other fibres which undergo microstructural changes during heat treatment, the focus of attention was to determine the temperature regions in which the necessary fibre changes took place.

Unlike the cold-drawn fibres, in which shrinkage is a useful criterion of set, cellulose triacetate shrinks relatively little, and consequently it was not found possible to use shrinkage as a measurement of degree of set. As thermally induced changes of the microstructure of fibres generally require a degree of molecular mobility, an approach was made to the problem by measuring the extension characteristics of yarns under small static load (0·2 g./denier) at high temperatures. Under these conditions it was found that the yarns began to extend at approx. 170°c. The extension increases progressively until 210–220°c. is reached, after which no significant changes take place.

Similar experimental work carried out in a pressure steam chamber showed that extension took place at much lower temperatures, a measurable extension being obtained as low as 105°c. and the maximum extension being reached at 120–125°c. From this work the range of operative setting temperatures was determined, which have since been confirmed in bulk practice.

As a practical everyday tool, extension techniques leave much to be desired, and are unlikely to find much practical application. Since the investigation was carried out to determine the best conditions for finishing rather than as a fundamental study of fibre properties, additional methods of following the progress of fibre consolidation with setting temperature were needed. It is well known that a decrease in porosity of a fibre (usually reflected in a reduction of the water imbibition) is generally accompanied by a reduced uptake of dyes. It was found that under conditions of dry heat setting the affinity of the fibre for disperse dyes becomes perceptibly reduced at 160°c., and falls steadily with further increase of temperature. Similar behaviour is shown by fabrics which have been preheated with steam under pressure. Where it is necessary to investigate the effect of setting conditions, dye absorption techniques provide a relatively simple method of arbitrarily assessing the degree of set. The test is, for obvious reasons, restricted to fabrics which are undyed.

The reverse procedure, that of desorption of dyes, can also be used for following the effect of setting temperature. The technique used at Coventry for this purpose employs a standard fabric which has been dyed (preferably at 80–90°c.) until filament penetration is complete (this minimises effects due to further diffusion of dye). As the setting treatment results in the entrapment of the dye molecules, the rate of desorption of the dye is decreased, and this affords an indication of the degree of set. Since desorption of dyes into aqueous baths is too slow to be of practical value, the preferred method of measurement is to use a solvent which has a slight swelling action on the fibre, e.g. trichloroethylene. As set fibres apparently swell more slowly than unset ones, the leaching of dye from the latter is distinctly greater.

Although both dye absorption and dye desorption tests are extremely useful where rapid assessment is required, they depend upon inference for their interpretation, and are, therefore, not absolute. A more fundamental approach has been developed by British Celanese Ltd. This is based upon the fact that an increase of the crystalline order of the fibre enhances the resistance of the fibre to further thermal deformation, and set fabric exhibits a substantially increased resistance to filament adhesion and fusion when heated beneath a metal plate at high temperatures. The increased resistance can also be used as a criterion of set. We may eventually anticipate more absolute forms of measurement, perhaps by change of density or other basic physical properties.

Some clarification is required of the sequence of finishing operations necessary to use the thermoplastic properties of Tricel to the maximum for giving set-flat, embossed, or pleated effects. Firstly, however, one has to decide at what stage of fabric processing these finishes are applied.

Mechanical finishes, such as embossing and pleating, are carried out as a final finishing operation, but setting may be carried out at various stages during the processing.

The industry is at present equipped with high-temperature stenters to preset nylon and polyester fabrics, and for this reason it is convenient to set fabrics in the grey. Setting at this stage has other advantages: for instance, fabrics which have to be processed in rope form are less prone to creasing during winch treatment when they have been set prior to dyeing. In view of the fact that a slight yellowing takes place during presetting— as a result of oxidation— this setting prior to bleaching is a natural sequence, as the yellowing can be removed during subsequent wet processing by bleaching or oxalic acid scour—

Hydrochloric acid (14°Tw.)	3/1000
Oxalic acid	2/1000

for 1 hr. at 70°c. followed by a thorough wash-off. Another advantage to be gained from presetting is that allowance for change in colour of dyed fabric does not have to be made by the dyer, for he can match directly to pattern.

As with other fibres, which are preset in this way, it is imperative to ensure that the size is not fixed during setting, and that the fabric is free from sighting colour and loom stains, which will be fixed during this operation. In such circumstances as these it is essential to set after efficient desizing, a process which has a certain nuisance value, as it entails an extra drying operation.

It has already been mentioned that efficiently set fabric has a lower affinity for disperse dyes, and also that setting improves the fastness to washing— and to a certain extent gas-fume fading— and it is natural, therefore, that when one is producing heavy depths and requires a high degree of wet fastness consistent with the more frequent washing which "easy-care" allows, postsetting should be resorted to. Setting of fabric as a final operation is also essential to fix effects produced by mechanical deformation of the cloth— by embossing or by local mechanical shrinkage.

It must be borne in mind that dyeing must be carried out with dyes which have been selected to give a minimum change in colour during postsetting.

It has been pointed out, from measurements of fibre flow in steam, that the use of this medium for setting is by far the most satisfactory, for the following reasons—

(1) It gives the maximum resistance to wet creasing, which is an essential aspect of a smooth-drying fabric

(2) There is no filament adhesion, which could result from the application of heat in the absence of moisture

(3) The degree of tendering of the fibre is far less than that which takes place when Tricel is heat-set in the absence of moisture under conditions essential to give the maximum amount of fibre consolidation

(4) A marked increase of washing fastness of dyes ensues, which is essential for garments washed more frequently.

The greatest difficulty encountered with steam setting is that with the plant available today it must of necessity be a batch process. The type of apparatus found most satisfactory is an autoclave. This is preferably attached to a vacuum pump, and the sequence of operations controlled with a cycle controller in order to ensure uniformity of results.

The procedure is to dress the fabric on to a perforated tube and subject to saturated steam at 20 lb./sq.in. pressure for 15–30 min. depending on the quantity of fabric and the thermal capacity of the system. In order to obtain efficient penetration of the steam, prior evacuation (down to 26 in. mercury) is essential.

Other factors which affect penetration are the number of layers of fabric on a tube and the tension under which they are wound. The thickness of the package and the tension can be reduced by using as large a diameter tube as convenient, and dressing one piece only per tube. Aluminium tubes of about 9 in. diameter have been found to be convenient.

Uniform penetration by steam of the roll of cloth is particularly important when fabrics are set prior to dyeing. (It has been previously pointed out that setting affects the dyeing affinity of Tricel to various degrees, depending on the extent of setting.) Minimum tension is essential in order to avoid watering of the fabric. It is also essential to avoid condensation spots on the fabric by efficient insulation of the vessel and by preheating the perforated tubes.

All setting operations impart a slight yellowing to Tricel resulting from oxidation. On steam setting this yellowing can be minimised by re-evacuation after a few minutes' steaming.

Steam setting can be carried out at any stage of processing where appropriate.

Knitted fabrics lend themselves particularly to steam setting, although many woven fabrics can be set by this method. Spun shirting fabrics containing Tricel and Fibro can be stabilised by this method, whilst foulards and shantungs retain the typical soft, crisp handle usually associated with secondary cellulose acetate.

Tubular-knitted fabrics may be finished after dyeing, on a combined drying and finishing machine, and collected on a cardboard tube of 2–3 in. diameter, which can then be inserted into an autoclave for setting, following which it can, after suitable inspection, be despatched, a very simple sequence of operations.

The decatiser can be used to give a certain measure of set and can be applied to some Tricel

filament cloths (crêpes, etc.) at any stage during processing. It is particularly beneficial to fabrics which have been set in hot air at some previous stage of preparation, as it removes filament adhesion and contributes to resistance to wet creasing. The duration of blowing should be longer than is normally given as a finishing operation. A satisfactory procedure is to steam at 80 lb./sq.in. pressure for 10 min.

Alternative methods have been used in Europe and in America for setting certain types of triacetate fabrics. In America the Burlington pressure dyeing machine has been installed widely for the dyeing of polyester fabrics. This is an enclosed pressurised apparatus in which the dye liquor is circulated through the fabric, which is wound on to a perforated tube. Dyeing can be carried out at temperatures over 100°c. Other machines which perform the same operation are the Belfours (Germany) and the Clermont-Bonte (France). It is clear that such a machine lends itself to simultaneous setting and dyeing, but is applicable only to fabrics of an open nature, such as ninons, crêpes, and knitted fabrics. It is essential that the fabric be dressed on to the tube accurately, crease-free and with minimum tension, in order to avoid watering. This being so, a short stenter must be used for batching; this should have suitable selvedge uncurlers for dressing knitted fabrics.

The process has been found useful for the setting and dyeing of fabrics in pale colours, watering being more evident in deep colours. As with all circulatory dyeing machines, precautions must be taken to avoid the deposition of soiling matter.

Although setting with steam is a far more efficient method than the application of dry heat to fabric, it is more restricted in application, because all methods in use depend on treatment of the fabric in batch form, and the circulation of steam or water through the fabric in roll form. This limits the range of fabrics to open structures which are permeable in roll form. There is clearly a need for apparatus which applies saturated steam at temperatures over 120°c. to fabrics in a tension-free state continuously.

Experiments are in progress on such an apparatus. It consists of a travelling brattice, mounted between two chambers with transverse slots of a high-velocity slack drier. The air supply is recirculated through an electric heater. Steam is admitted into the system to give a high degree of saturation at the temperature required. This apparatus has proved to be extremely useful, and in fact the only suitable apparatus for setting embossed patterns of a three-dimensional nature, which cannot be handled in roll form owing to the difficulty of preventing the pattern being distorted whilst the fabric is dressed on a roller or tube. It is only to be expected that, with this degree of efficiency, one would persevere with this machine with a view to using it to set woven cloths of a type hitherto not possible.

Whilst the next stage in the development of a continuous steam setting apparatus is not quite clear, it is possible that efficient means of accomplishing this may be achieved by suitable modifications to orthodox high-temperature superheated-steam slack-drying equipment.

Stenters built or adapted to set polyamide or polyester fabrics can also be used for setting Tricel fabrics. As fabrics made from Tricel do not shrink when heat-treated, certain precautions must be taken to prevent extension. Excessive pressure on one surface of the fabric resulting from unbalanced air flow must be avoided, or fabric width cannot be controlled (wide or heavy fabrics should for this reason be supported by rollers during stentering).

A satisfactory setting procedure is to stenter at 200°c. for 25 sec.: stentering at a higher temperature may give the fabric better resistance to glazing at the sacrifice of some strength loss.

Preset fabric as removed from the stenter may feel firm and appear slightly parchment-like as a result of filament adhesion. This stiffness will be removed during subsequent processing, the first stage of which should consist of a thorough wetting-out of the cloth at open width to ensure swelling of the filaments.

It is beneficial to introduce moisture into the system during stentering, as the presence of superheated steam will—

(*a*) Enable a lower setting temperature to be realised

(*b*) Assist in preventing filament adhesion by acting as a lubricant

(*c*) Reduce yellowing

(*d*) Increase the resistance of the fabric to wet creasing.

Filament adhesion occurring on postset fabrics may be removed by means of a button breaker, knife calender, or by decatising; wetting out in a softening agent is also beneficial.

Two other methods are in current use for setting polyamide and polyester fabrics and are applied for setting triacetate abroad. Hot-roll setting, based on the National Drying Machine Co. and Morrison Machine Co.'s cylinder machines, is carried out in America on woven fabrics, although there is little experience of this system in this country.

The Bates Model K high-temperature blanket calender has been used in this country for setting knitted fabrics. The procedure is to run the fabric at 15 yd./min. (giving a time of contact of 4–5 sec. at 200°c.). Roll setting imparts similar properties to Tricel to those resulting from stenter setting, but like stenter setting it does not materially reduce the resistance to wet creasing. Roll setting of knitted fabrics has the advantage over stenter setting that the fabric can be set under tension-free conditions. This ensures that there is less filament adhesion and less reduction in strength during setting.

EMBOSSING

As Tricel is the least expensive thermosetting fibre on the market at the present time, its potentialities in the field of thermally applied modifications of fabric surfaces and of sculptured effects are

considerable. The procedure must, however, take into consideration the characteristics of the fibre, and bruising of the filaments by the application of excessive heat and/or mechanical pressure must be carefully avoided. The preferred conditions are, therefore, a relatively low mechanical pressure and temperature, and for development work we generally use pressures of 12–20 lb. per linear inch and temperatures in the region of 110–120°C.

As in the case of pleating, it is necessary to set at some stage during the process. In the case of superficial effects (e.g. crystal patterns and ciré) it is possible to emboss the fabric either before or after dyeing, but as a general rule pre-embossing is limited to fabric which can be processed on the winch. The embossing of superficial designs is a relatively simple procedure, and is already practised on a commercial scale.

The embossing of deeper and sculptured effects presents rather more difficult problems, and it is important that the construction of the fabric is suitable for the design being applied. It is essential that fabrics intended for deep three-dimensional designs should have sufficient crimp in the warp and weft yarns to allow for stretching, otherwise filament breakage will occur. Fabrics for this purpose are preferably as near to square in construction as possible. Where the construction of the fabric is unsuitable, breakage of the fibres and filaments will take place, and this breakage can be accentuated if the fabrics are preset.

Deep embossing invariably results in slight glazing and filament adhesion, and as these are not permanent and are removed by mechanical agitation or mild washing, it is necessary to take steps to remove these undesirable characteristics. The preferred approach is to post-steam the fabrics, a process which has the function of eliminating filament adhesion, effecting consolidation of the fibre structure, and fixing the design.

The actual steaming of deeply embossed fabrics has presented some problems, mainly on account of the fact that steaming in the roll form frequently results in distortion of the package. The brattice machine previously described is being used for development work.

PLEATING

In the field of durable pleating, cellulose triacetate fibres are already firmly established, and subject to an adequate Tricel content and suitable construction, satisfactory wash-and-wear performance is assured.

The actual operations of machine and hand pleating are well known, and a discussion of the practical aspects would, therefore, be superfluous. Nevertheless, several aspects of the pleating process, particularly the evaluation of pleated fabrics, have presented some interesting problems. It has been found, for example, that the maximum machine pleating temperature is in the region of 170°C., as above this point glazing takes place. This shows an excellent correlation with work on the extension of yarns under small load and corresponds to the point at which initial extension of the fibres is observed. As the investigation of the plasticity and flow characteristics of cellulose triacetate yarns was carried out as long ago as 1950, it is gratifying to note that experiments requiring only a gram weight and some bobbins of 55-denier yarn have so fully justified themselves in actual practice. This merely emphasises the fact that investigations of the properties of fibrous materials are often within the scope of even a moderately equipped dyehouse laboratory.

The actual assessment of pleated fabrics, particularly from the point of view of quality control, presented even more intricate problems. The load required, for example, to stretch a fabric to 100% of its pleated length is extremely small, being of the order of 3×10^{-4} g./denier, when measured in the wet condition. As far as current knowledge goes, no instrument for measuring the load–extension characteristics of pleated fabrics has so far been devised, which emphasises the difficulties of measuring forces of this order. However, as subjective assessment (simple hand washing and visual assessment) had proved to be unreliable, it was necessary to devise a more objective test.

As a pleated fabric can be regarded as a delicate elastic system which is subject to stress–strain decay, any quantitative test must necessarily take into account the fundamental properties of such a system. It follows from elementary considerations that the performance can be defined by—

(a) Measurement of the strength of the system, i.e. the pleat strength, and

(b) By determining its susceptibility to stress–strain decay.

For the measurement of pleat strength, extension of the pleated fabrics, under either their own weight or an applied load, can be used. Fabrics of low pleat strength give a relatively high extension, and *vice versa*.

The preferred method is to subject a pleated strip of fabric of known pleat frequency and dimensions to a washing test in which the strip is hung from an arm which reciprocates at a rate of 3,200 strokes per hour, the pleats being in a horizontal position. The strips are then hung to dry for 24 hr., after which the extension is measured. Under these conditions we have a method in which the load applied is proportional to the combined weight of the water held by the fabric and that of the fabric itself.

For the determination of stress–strain decay characteristics, measurement of the elastic recovery of a fabric after extension in water under defined conditions may be carried out. It will be appreciated that in a hypothetical assemblage of fibres made from a highly elastic material such as rubber, recovery of the original configuration after stretch would, to all intents and purposes, be complete. With assemblages of fibres this is not so, particularly when the pleated material is extended in the wet state, and the contraction of a fabric therefore provides an arbitrary measure of susceptibility to stress–strain decay. Nevertheless, the contraction of pleatable fabrics is of such an order as to be easily measurable.

The test method used consists in stretching a strip of fabric of known pleat frequency and

dimensions to double its original pleated length, and placing in water at 50°c. for 30 min., whilst maintained in the stretched condition. The cutting is then removed from the bath, and released from its clamps, after which it is allowed to contract on a glass plate for 24 hr. Mercury can also be used instead of the glass plate; this is a more ideal surface on which to carry out such tests.

The results of both tests are combined to give what is provisionally known as the "pleat retention index". Several forms of numerical treatment of the results are possible, the discussion of which is outside the scope of this paper. A convenient one is to use them in the form C/E, where C is the contraction and E the extension. This follows from the fact that the desiderata for good pleat retention are low extension (i.e. high pleat strength) and high contraction.

Not infrequently in the physical testing of textiles figures are obtained which have an indeterminate relation to actual subjective assessment, and the interpretation of such results in terms of their subjective significance is often a very difficult problem. One has only to cite abrasion tests as a particular example.

With this in mind, and in order to bridge the gap between test results and visual assessment, approx. 30 fabrics were assembled, and the indices determined. Pleated and washed samples were examined individually by 20 observers, who were asked to pass, rate as doubtful, or reject, in terms of acceptability. From this trial it was possible to derive a near quantitative assessment of the probable level of consumer acceptance. Since the inception of the test, a great deal of data has been obtained on fabrics which have either failed or succeeded in the commercial sense, and the information obtained on the industrial scale has largely confirmed the original experimental work.

* * *

The authors wish to thank the Directors of Messrs. Courtaulds Ltd. for their kind permission to publish this paper.

COURTAULDS LTD.
COVENTRY

(*MS. received 15th July 1958*)

COMMUNICATION

Adsorption at Organic Surfaces

V—A Study of the Adsorption of Dyes and Other Organic Solutes by Cellulose and Chitin

C. H. GILES and A. S. A. HASSAN

Adsorption experiments with cellulose and chitin and a variety of solutes, including non-ionic hydroxy compounds, aromatic sulphonic acids, and azo dyes, are described. In non-aqueous solvents the non-ionic compounds are adsorbed by both substrates, but in water they are adsorbed only by chitin. Almost all the sulphonated compounds are adsorbed by both substrates, but benzenesulphonic acid is not adsorbed by cellulose.

It is concluded that cellulose adsorbs by hydrogen bond formation with the solute in absence of water, but in presence of water by van der Waals attraction alone. Chitin can adsorb by both of these mechanisms and also by ion exchange. In chitin the active centres for both hydrogen-bond and ion-exchange adsorption are the acetamido and amino groups; the hydroxy groups in both cellulose and chitin are believed to be strongly solvated in water, and unable to adsorb solutes by hydrogen bonding.

The affinity for cellulose of the aromatic solutes and of vat dyes for which published data are available increases linearly with the logarithm of the length of the conjugate chain in the molecule. This appears to confirm that the affinity represents the attraction between the cellulose chain and the π-electron system of the solute molecules, which must be planar to have high substantivity. The effect on affinity of the amido group is discussed.

Introduction

Previous papers have described a survey of the adsorption properties of chitin for inorganic and organic acids [1], and for sulphonated azo dyes [2]. The present investigation compares its adsorption properties for several solutes with those of cellulose.

Chitin is one of the most important natural structural materials, forming the principal constituent of the exo-skeleton of insects and crustaceae [3, 4]. It is usually regarded as a polymer of N-acetylglucosamine [3–6], i.e. a form of acetamidocellulose, though analytical data are consistent with a slightly modified form of this structure, in which a small proportion of the amino groups (about 13%) are unacetylated and free [1]. An examination of hydrogen-bonding reactions in water [7–9] has revealed differences in behaviour between cellobiose (or glucose) and N-acetylglucosamine. The hydroxy groups (and ether oxygen atoms) in both types of compound are unreactive in water, but N-acetylglucosamine can form complexes in neutral solution or at pH 9·0 with other solutes, probably by reaction of its $\rangle$NH group. These two compounds can be regarded as models for cellulose and chitin respectively, and it is therefore likely that in water hydrogen bonding may contribute to the affinity of solutes for chitin, but not for cellulose. The previous investigations [1, 2] gave no evidence that hydrogen bonds contribute significantly to the affinity of aromatic solutes for chitin in acid solution. Under acid conditions, however, the potentially hydrogen-bonding groups in the solute are in competition with hydrogen ions for the same sites—the acetamido and amino groups—and this could account for the effects observed.

The previous results suggested that adsorption of anionic aromatic solutes by chitin under acid conditions is largely an ion-exchange process, assisted by van der Waals attraction between the aromatic nuclei and the glucosidic residues of

the chitin molecular chains. In the present experiments anionic aromatic solutes have been applied to chitin and cellulose under neutral or weakly alkaline conditions. Under these conditions the basic groups in chitin will remain uncharged, and ion exchange will thus be suppressed, and since cellulose has no ionisable groups, any differences in adsorption behaviour between the two substrates may be attributed to variations in van der Waals and hydrogen-bond forces. Chitin would be expected to exhibit considerably more powerful hydrogen-bond attraction than cellulose, but rather lower van der Waals affinity, because its molecular chain has a more uneven contour, owing to the pendant acetamido groups.

Apart from the earlier papers [1, 2] and a brief preliminary account of some of the present investigations [9], Hackman's report [10] on the adsorption of protein is apparently the only other detailed quantitative account of the adsorption properties of chitin. Knecht and Hibbert [4] gave a very brief description of its dyeing properties.

Experimental

MATERIALS

The cellulose was Courtaulds' bright viscose rayon (Fibro), 4·5 denier, 6-in. staple. This was lightly scoured before use in a solution containing 3 g. anionic detergent (Lissapol C, ICI) and 2 g. sodium carbonate per litre at 80°c. for 1 hr., then well rinsed in cold water containing a little dilute acetic acid, oven-dried at 100°c., and conditioned in air for 48 hr. before use.

Chitin was prepared as previously described [1] by Thor's method [11] from the shells of the Norwegian lobster (*Nephrops norvegicus*).

Benzene was dried over sodium; all water was distilled; the buffer solutions were prepared from commercial buffer tablets (Marconi Instruments Ltd.). Most of the solutes were obtained from commercial sources and purified in the laboratory; some of the dyes were prepared in the laboratory. Anthracene-1-sulphonic acid was made from the anthraquinone compound by reduction with zinc dust and ammonia. The samples of sulphuric esters of leuco vat dyes were obtained in the form of suspensions of the sodium salts in 5% sodium carbonate solution. The cetyl alcohol used consisted of "technical grade" crystals.

The solutes used included hydroxy compounds, sulphonic acids, and azo dyes, and are listed in Table I.

ADSORPTION TESTS

For each test, a 0·1-g. sample of chitin or viscose rayon and 10 c.c. of solution were placed in a sealed glass tube and tumbled under water in the thermostat, the viscose rayon fibre being first placed in a perforated glass tube to ensure adequate penetration of liquid [12]. Preliminary rate tests were made to find the time required to reach equilibrium when determining isotherms, as already described [1].

ANALYSIS

Phenol in *iso*octane solution and all the coloured substances were determined colorimetrically on either a Hilger Spekker photoelectric absorptiometer or a Unicam photoelectric spectrophotometer (SP 500 or SP 600); phenol in aqueous solution was determined volumetrically by the bromate–bromide method, and resorcinol by potassium permanganate titration. The purity of the dyes was determined by titanous chloride titration.

Stuart-type molecular models (Catalin Ltd.) were used in estimating the probable orientation of the cellulose chain relative to the dye molecules, and hence the effective bond-lengths of the dyes.

For comments on the level of precision of the adsorption measurements, see the previous paper [2].

MEASUREMENT OF AFFINITY

The affinity of some of the compounds used for viscose rayon in the present work has been calculated from the expression [13, 14]—

$$-\Delta\mu = \boldsymbol{R}T\{\ln [\mathrm{D}]_f + z \ln [\mathrm{Na}]_f - \ln [\mathrm{D}]_s - z \ln [\mathrm{Na}]_s - (z+1) \ln V\}$$

where $[\mathrm{D}]_f$ and $[\mathrm{D}]_s$ are the concentrations of dye in the fibre and in solution respectively, $[\mathrm{Na}]_f$ and $[\mathrm{Na}]_s$ are the corresponding sodium ion concentrations, and z is the valency of the dye anion. V is the "volume term", representing the effective volume of water in the substrate (in litres/kg.); the value of 0·46 is used here.

The concentration of sodium ions in the fibre was calculated from the expression derived from the Donnan equilibrium—

$$[\mathrm{Na}]_f = \tfrac{1}{2}\{z[\mathrm{D}]_f + (z^2[\mathrm{D}]_f^2 + 4V^2[\mathrm{Na}]_s\,[\mathrm{Cl}]_s)^{\frac{1}{2}}\}$$

where $[\mathrm{C}]_s$ is the concentration of chloride ions in the external solution, dyeing being carried out in presence of an excess of sodium chloride.

For each dye one solution was used, of a concentration chosen to give an adsorption value well below saturation, and the affinity was calculated from the equilibrium concentrations of the dye in fibre and in solution.

Affinities for chitin were not determined, because no value for V is available.

Apparent heats of adsorption were computed from the isotherms by the use of the Clausius–Clapeyron equation.

Results and Discussion

Table I gives a summary of the results, and adsorption isotherms and other data are given in Fig. 1–14 and Tables II–V.

The results may be summarised briefly as follows—

ALCOHOL AND PHENOLS

Methanol is adsorbed by cellulose and chitin from non-aqueous solution (Fig. 1). Phenol is adsorbed by viscose rayon from non-aqueous solution (H. R. Chipalkatti, private communication) and by chitin also (Fig. 2), by which it is adsorbed in greater amount than methanol, an indication of penetration into more crystalline regions, and thus of the higher affinity of the phenol–chitin compared with the alcohol–chitin bond*.

* Cf. the free energies of formation of bonds (by dimethylformamide in CCl_4) with phenol and benzyl alcohol, viz. −3·23 and −2·23 kcal./mole respectively (Flett [15]).

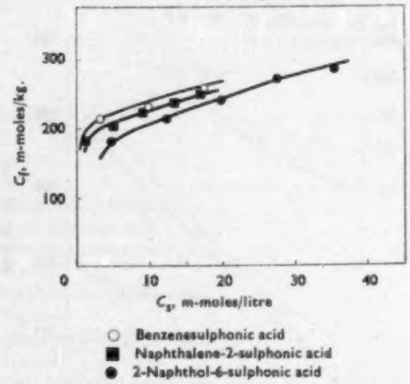


FIG. 6—Adsorption of Sulphonic Acids on Chitin at 50°C.

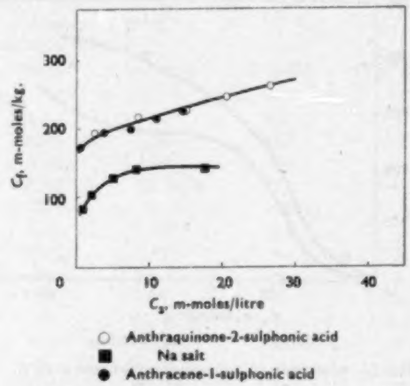


FIG. 7—Adsorption Isotherms on Chitin at 50°C.

(judged by the equilibrium concentration of the bath at, say, 50% of the saturation adsorption value) increasing with the number of nuclei (Fig. 5). Benzenesulphonic acid and its sodium salt are not measurably adsorbed.

On chitin these acids and their sodium salts are readily adsorbed from unbuffered solutions (Fig. 6 and 7). All of them are in fact adsorbed in very similar amounts, and the operation of the enhanced physical attraction of the larger molecular area or conjugation is not immediately apparent. In fact, adsorption tends to fall a little with increase in molecular size. Nevertheless the enhanced attraction probably is operating; this will be clear from a study of Fig. 5 and the accompanying discussion in the first of these three papers[1]. Briefly, the expected increase in adsorption with molecular area is offset by the high crystallinity of chitin, which offers increased resistance to penetration of solute molecules as their volume increases.

A few tests were made in solutions buffered to pH 9, and comparative data, read by interpolation from the isotherms, are given in Table II [cf. 9]. At pH 9, all ion-exchange activity of chitin is suppressed, and in the absence of hydrogen-bonding groups in the solute, adsorption by either substrate can take place only by van der Waals attraction; it is clear from Table II that this attraction is more pronounced with cellulose than with chitin.

HYDROXYLATED SULPHONATES

The isotherms for the sulphonates of anthracene, anthraquinone, and alizarin on cellulose (Table II, Fig. 8 and 9) do not show any evidence that the strongly hydrogen-bonding (hydroxy) group in alizarin has any effect in increasing the adsorption. This group does, however, appear to influence adsorption on chitin*, and at pH 9 it raises the adsorption for chitin above that for cellulose (Table II). The quinone groups, which have weak hydrogen-bonding properties in water, appear to have little influence on adsorption.

β-Naphthol is not adsorbed by cellulose from 50% aqueous ethanol; probably its solubility is too high and its affinity for cellulose too low. Its 6-sulphonic acid is adsorbed from this solvent, perhaps because of its lower solubility in the bulk solution, or its more ready solubility in the solvated water surrounding the cellulose chains; Derbyshire and Peters[18] have suggested that the ionic groups in cellulose-substantive dyes raise their affinity in this way.

SULPHONATED AZO DYES

The adsorption of aniline→naphthionic acid (sodium salt) was compared with that of the corresponding "double" molecule Congo Red (benzidine→(naphthionic acid)$_2$) (Fig. 11). The two dyes have identical hydrogen-bonding groups, but the second dye should have much enhanced van der Waals affinity compared with the first, by virtue of its greater molecular area, linearity, and higher conjugation. At pH 9, ion exchange by

* The maximum adsorption of 2-naphthol-6-sulphonic acid is less than that of naphthalene-2-sulphonic acid, on both cellulose and chitin (Fig. 5, 6, 10). A likely explanation for the marked difference is that the hydroxy compound is dimerised by intermolecular hydrogen bonding. A dimer would have more restricted access than the monomer to chitin, and on both substrates reduced affinity would result from non-planarity of the two halves of the complex. In agreement with this suggestion, the solubility of the hydroxy compound was found to be lower than that of the other (38 and 192 g./litre respectively at 50°C.); it was in fact too low for a reliable molecular-weight determination to be made.

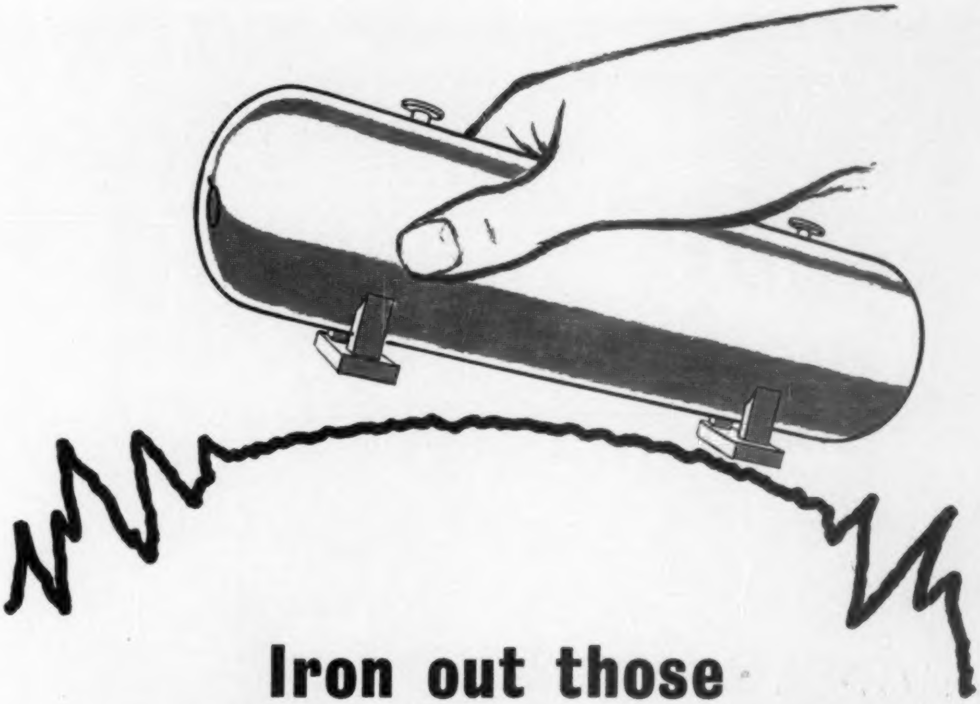
TABLE II

Comparative Adsorption Data for Sulphonates in Neutral and Alkaline Solution at 50°C.

Solute	Solvent	Substrate: Cellulose C_s*	Cellulose C_f*	Chitin C_s	Chitin C_f
Sodium naphthalene-2-sulphonate	Water	30	26	—	—
	pH 9 buffer	30	9·5	30	Nil
Sodium anthraquinone-2-sulphonate	Water	—	—	1·5	90
	pH 9 buffer	1·5	6·5	8	Nil
Sodium alizarinsulphonate	pH 9 buffer	1·2	8	1·2	22

* Equilibrium concentrations in bath (C_s mM.) and on substrate (m-mole/kg.).

face centre



Iron out those steam load fluctuations

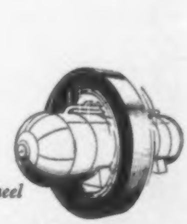
The installation of a RUTHS steam accumulator enables boiler plant to be run at a steady output giving maximum efficiency where there are widely varying steam demands. The accumulator also ensures a constant pressure in the process line at all times.

A RUTHS steam accumulator is essential where peak demands exceed the maximum which the boilers are capable of carrying and advantageous where smaller fluctuations in demand occur.

We would welcome the opportunity to investigate your problem and to submit proposals should we find that a case for steam storage exists.

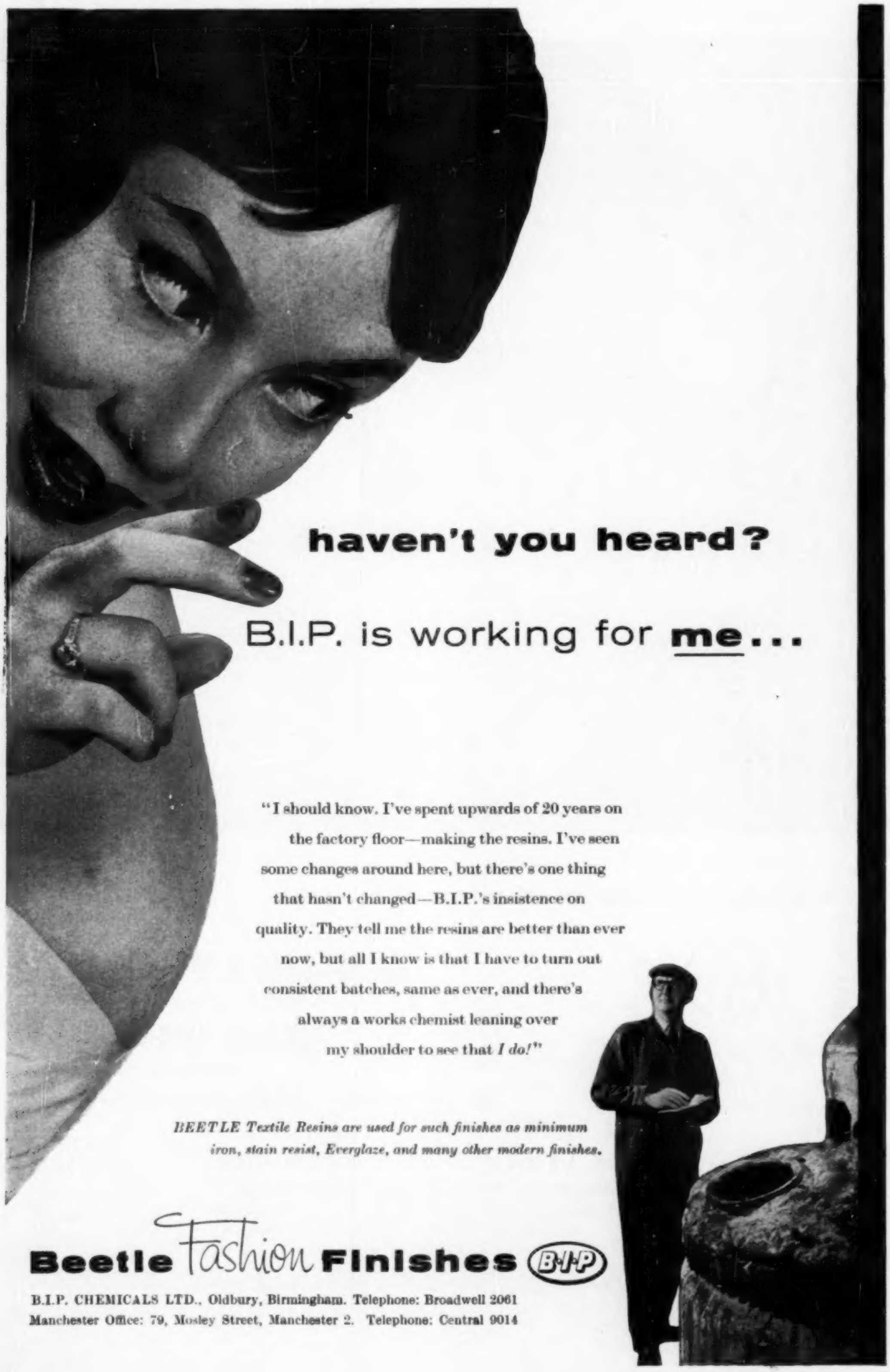
RUTHS
Regd Trade Mark

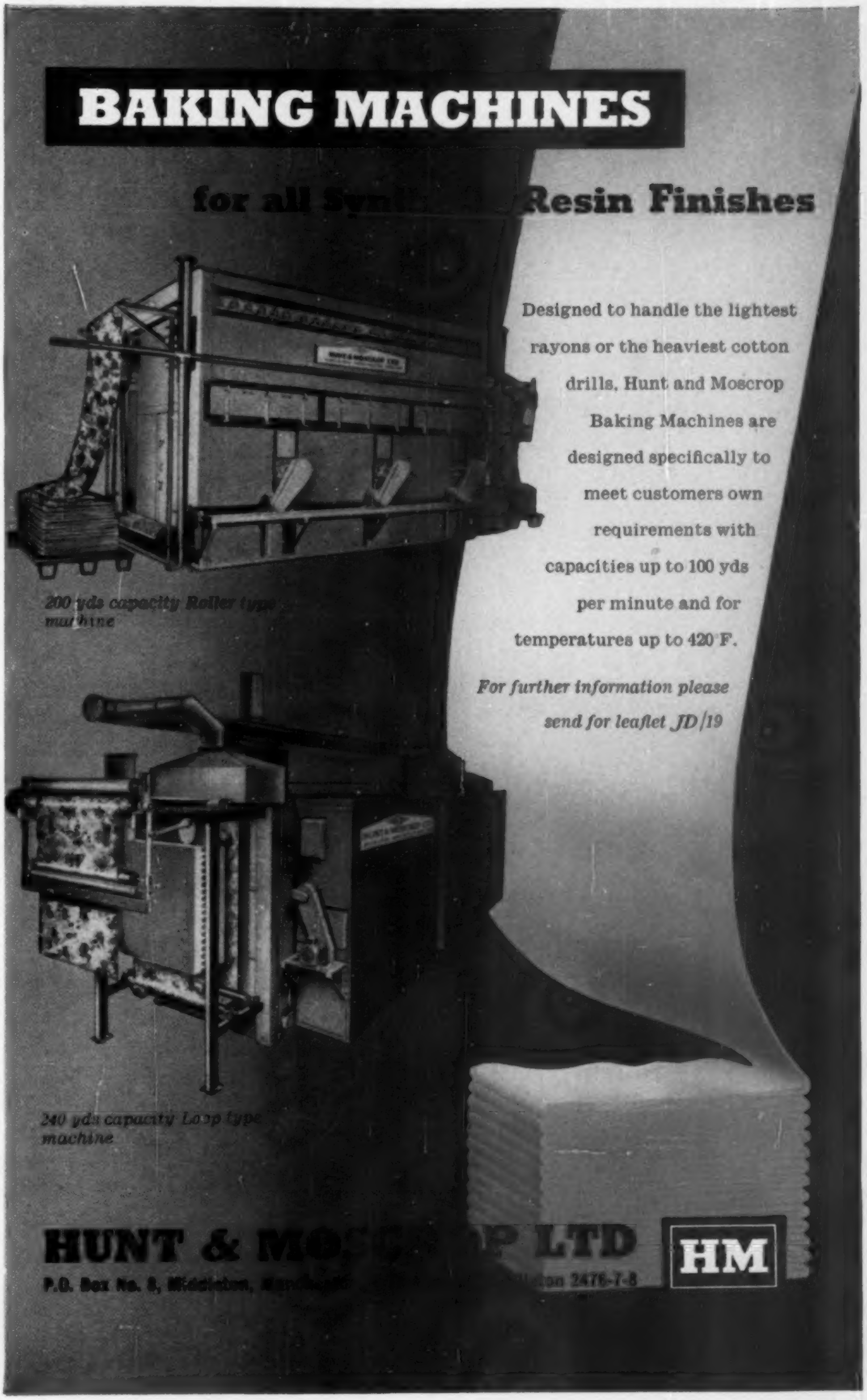
STEAM ACCUMULATORS



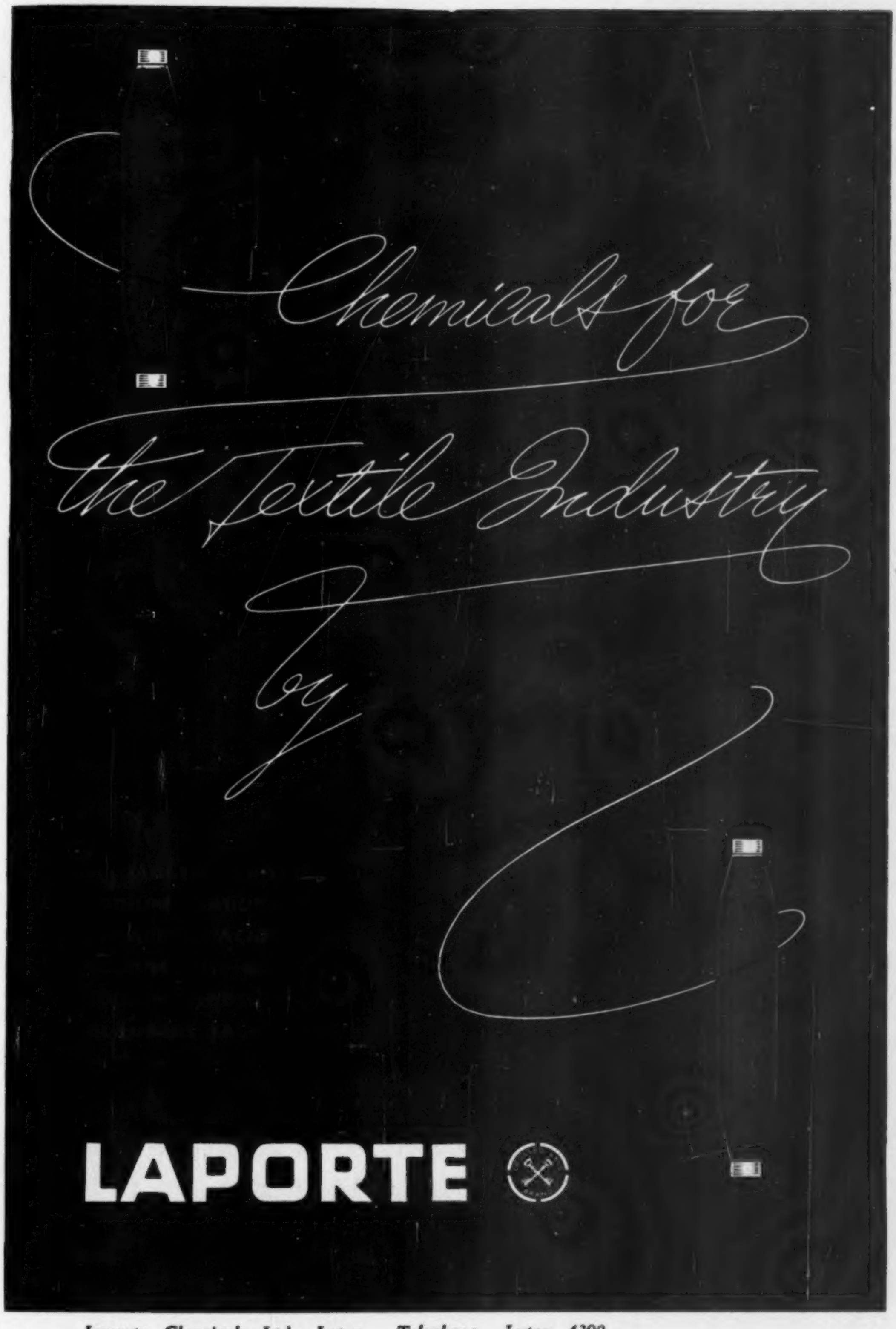
The Thermal Flywheel

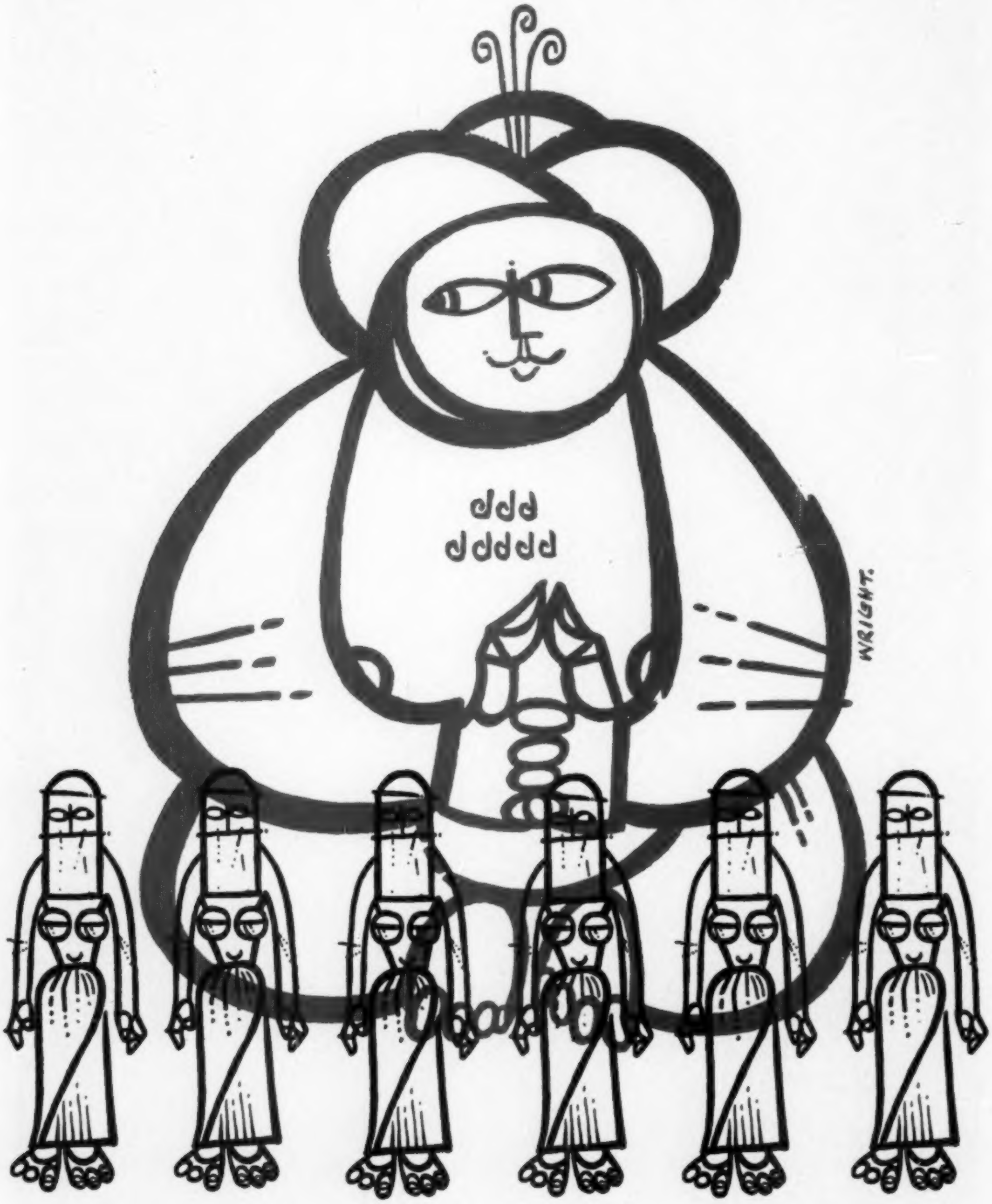
Cochran & Co., Annan, Ltd., Annan, Dumfriesshire, Scotland, and at 34, Victoria Street, London, S.W.1.
S/TAS/CH.635


haven't you heard?
B.I.P. is working for me...
"I should know. I've spent upwards of 20 years on the factory floor—making the resins. I've seen some changes around here, but there's one thing that hasn't changed—B.I.P.'s insistence on quality. They tell me the resins are better than ever now, but all I know is that I have to turn out consistent batches, same as ever, and there's always a works chemist leaning over my shoulder to see that *I do!*"
BEETLE Textile Resins are used for such finishes as minimum iron, stain resist, Everglaze, and many other modern finishes.
Beetle Fashion Finishes
B.I.P
B.I.P. CHEMICALS LTD., Oldbury, Birmingham. Telephone: Broadwell 2061
Manchester Office: 79, Mosley Street, Manchester 2. Telephone: Central 9014


BAKING MACHINES
for all Syn Resin Finishes
Designed to handle the lightest rayons or the heaviest cotton drills, Hunt and Moscrop Baking Machines are designed specifically to meet customers own requirements with capacities up to 100 yds per minute and for temperatures up to 420°F.
For further information please send for leaflet JD/19
200 yds capacity Roller type machine
240 yds capacity Loop type machine
HUNT & MO P LTD
P.O. Box No. 8, Middleton,
ton 2476-7-8
HM

dm/HM19


Chemicals for
the Textile Industry
by
LAPORTE


WRIGHT.

COLOURS

THAT LAST

The colour and pageantry of British ceremonial has lasted for centuries. So too have Chrome Chemicals in the production of colours that last. From the earliest Chrome mordants used with natural dyes to the premetallised synthetic dyes of today, Chrome Chemicals are still playing an important part in the production of dyestuffs and the colouring of textiles.

The scope of chrome dyeing is continually being broadened by new developments based on the consistent purity of chemicals produced by British Chrome & Chemicals. We are always happy to assist in such developments as well as supplying existing needs.

BRITISH

CHROME & CHEMICALS

LIMITED

A member of
Associated Chemical Companies Limited Group

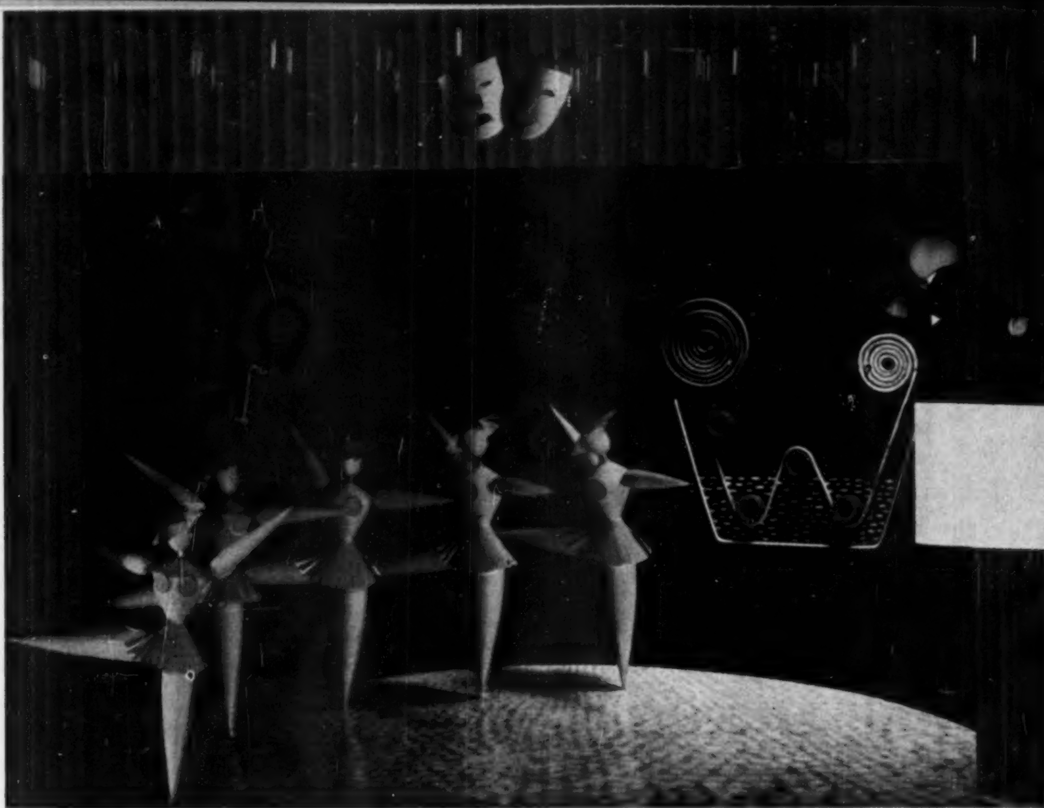
Manufacturers of: Sodium Bichromate, Anhydrous Sodium Bichromate, Potassium Bichromate, Ammonium Bichromate, Sodium Chromate, Potassium Chromate, Chromium Sulphate, Chromium Oxide, Chromic Acid.

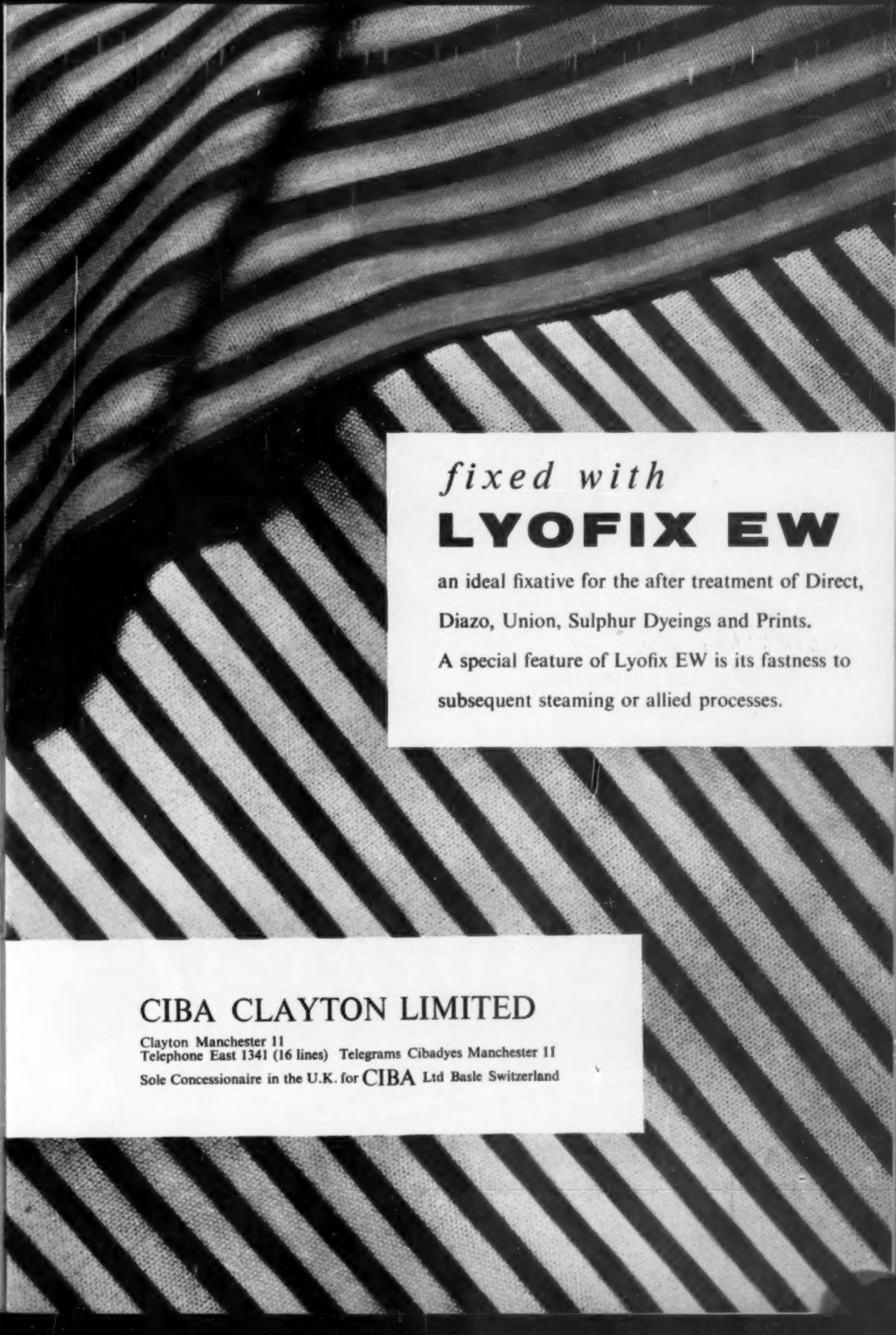
All enquiries to:

Associated Chemical Companies (Sales) Limited, P.O. Box No. 6, Leeds. Tel: Leeds 29321/8. Grams: Aschem, Leeds.

BCC 10682

1/506




fixed with
LYOFIX EW
an ideal fixative for the after treatment of Direct, Diazo, Union, Sulphur Dyeings and Prints.
A special feature of Lyofix EW is its fastness to subsequent steaming or allied processes.
CIBA CLAYTON LIMITED
Clayton Manchester 11
Telephone East 1341 (16 lines) Telegrams Cibadyes Manchester 11
Sole Concessionaire in the U.K. for CIBA Ltd Basle Switzerland


SULPHOSOL
SUITABLE FOR PAD JIG
PAD STEAM and
PACKAGE DYEING
Water soluble sulphur dyes giving
GOOD PENETRATION
BETTER HANDLE
EASY WASHING-OFF
LESS TROUBLESOME EFFLUENT
DYESTUFFS
JR &Co LTD

Your skill and new

brotasul

produce finer printing

Our new Brotasul is a formaldehyde sulphoxylate compound which has been designed to help you overcome certain difficulties associated with the more traditional sulphoxylates.

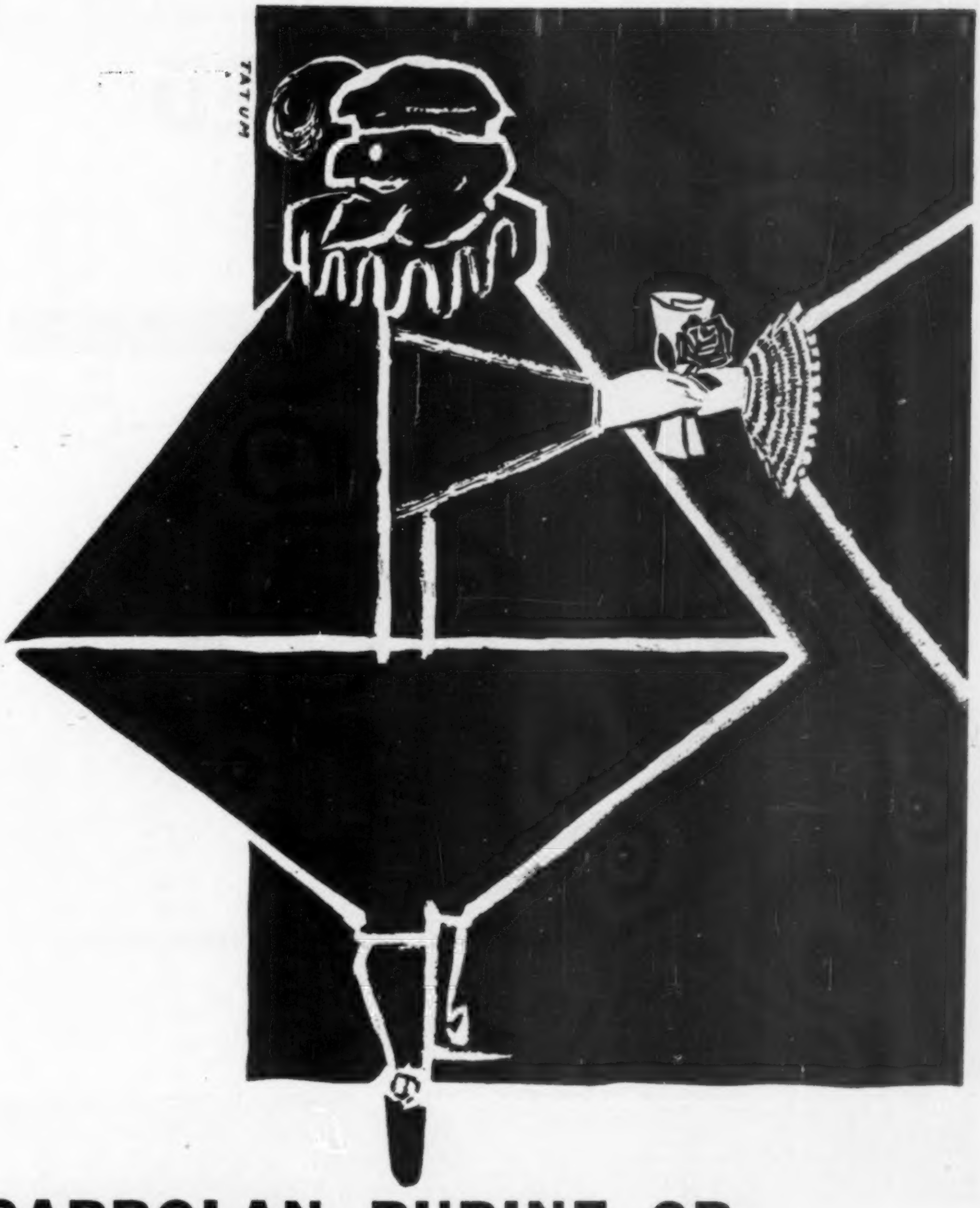
For example, there is no "halo" effect when Brotasul is used in the discharge printing of fine filament acetate fabrics. Brotasul offers advantages in the printing of fabrics containing fibres of cellulose acetate, triacetate, nylon, silk and wool. Brotasul has no tendering effect on wool, and it has a very low solubility.

May we tell you more about this new product? Please write to us for full information.

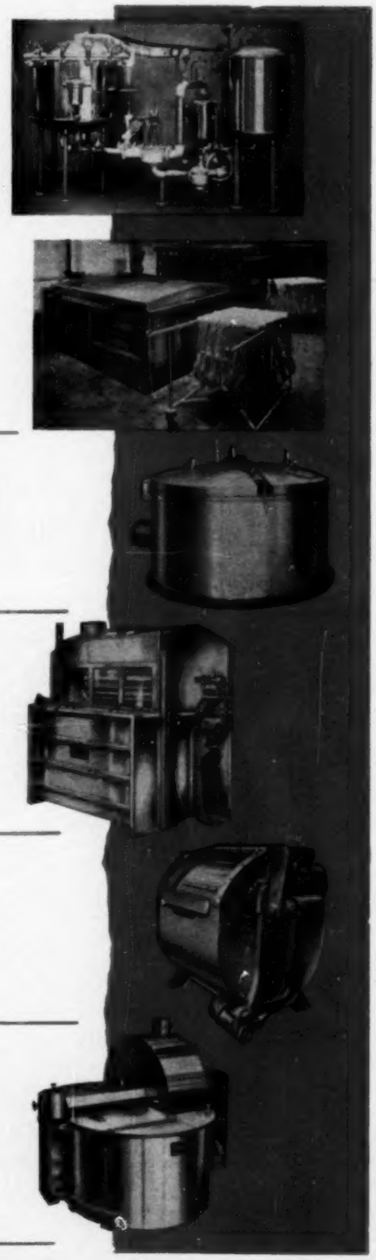
Brotasul by **Brotherton**

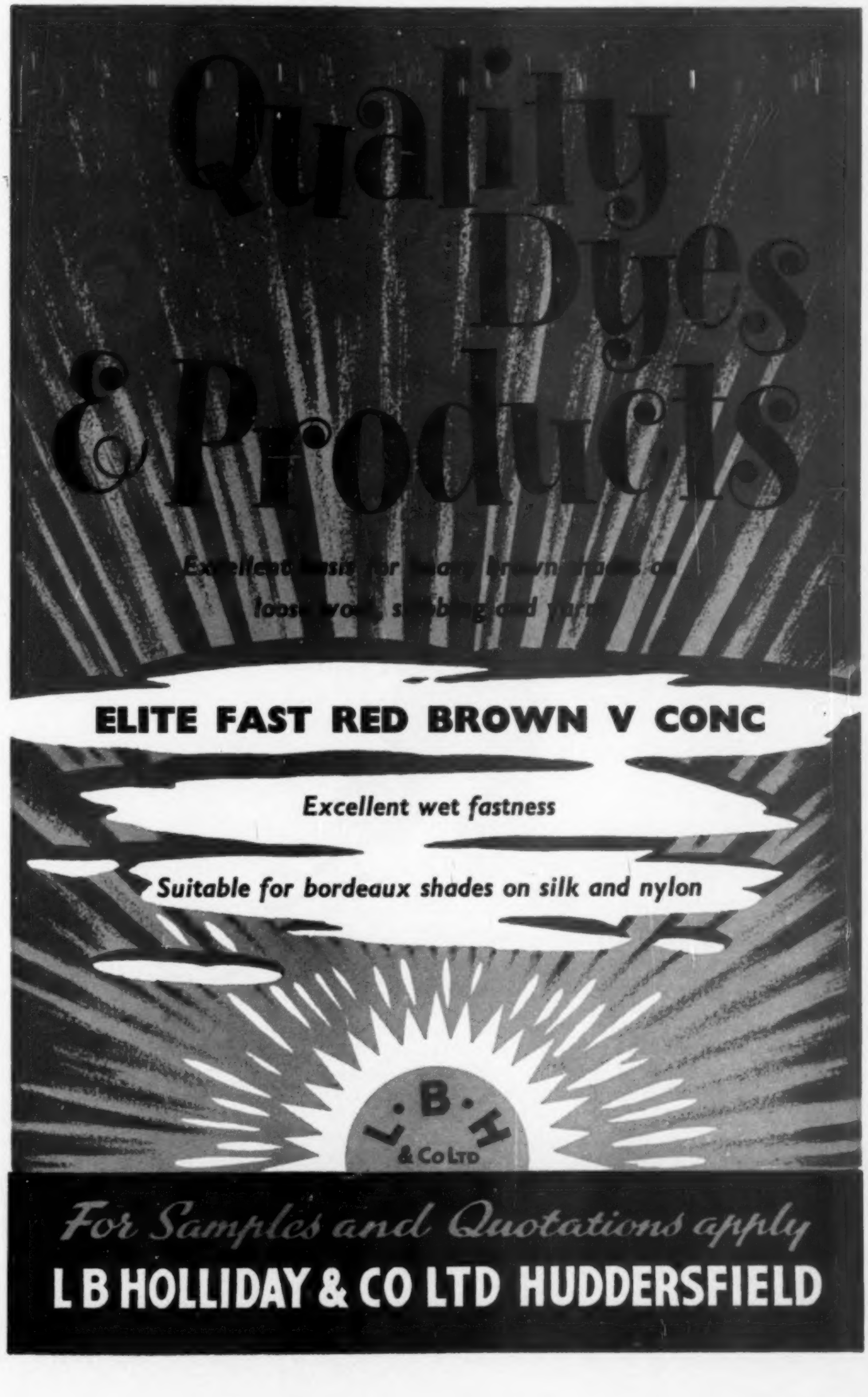
Brotherton & Company Limited is a member of the Associated Chemical Companies Group and all inquiries should be made to Associated Chemical Companies (Sales) Limited (the Sales Company of British Chrome & Chemicals Limited and Brotherton & Company Limited), at P.O. Box 6 Leeds

Telephone Leeds 29321-8 *Telegrams* ASCHEM LEEDS


TATUM


British Titan Products brighten products
BTP
TITANIUM PIGMENTS
All bright colours come from white
The beautiful tints of modern products
depend upon TIOXIDE Titanium Oxide
... the finest white pigment in the world.
BRITISH TITAN PRODUCTS COMPANY LIMITED
10 Stratton Street London W.1





Quality Dyes & Products
ELITE FAST RED BROWN V CONC
Excellent wet fastness
Suitable for bordeaux shades on silk and nylon
L.B.H & Co Ltd
For Samples and Quotations apply
L B HOLLIDAY & CO LTD HUDDERSFIELD


Richter

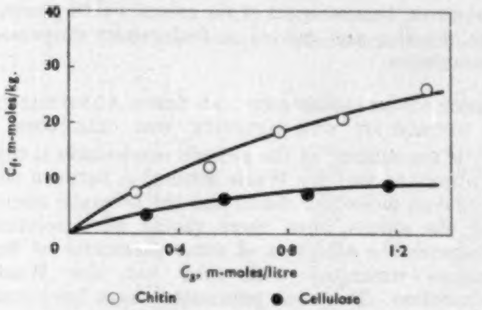


FIG. 8— Adsorption of Sulphonated Alizarin (C.I. 58005) from Water at pH 9 (50°C.)

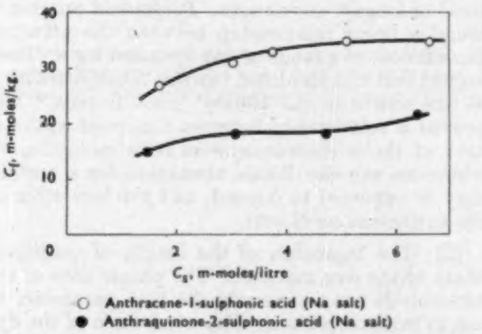


FIG. 9— Adsorption Isotherms on Cellulose from Water at pH 9 (50°C.)

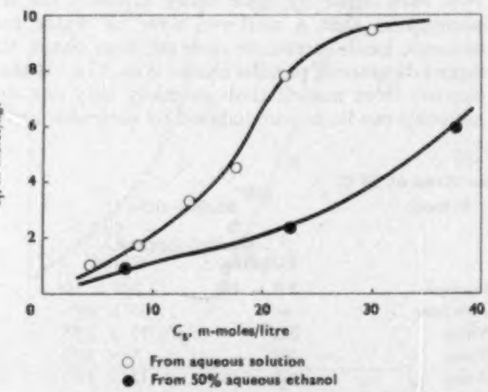


FIG. 10— Adsorption of 2-Naphthol-6-sulphonic acid on Cellulose at 50°C.

chitin being suppressed, the dye with the larger molecule is adsorbed a little more by this substrate than is the simpler dye (Fig. 11*b*); but from neutral and pH 9 solutions it is adsorbed to a considerably greater extent by cellulose (Fig. 11*a*). This is another indication that cellulose can exert stronger van der Waals attraction than chitin can, by virtue of the more regular outline of its molecular chain. If hydrogen bonding alone were the adsorptive force, both dyes should be adsorbed to a similar extent on cellulose. In neutral solution both dyes are appreciably adsorbed by chitin; here the mechanism is ion exchange [2]. Summarising the facts revealed in Fig. 11, it appears that on cellulose the determining factor in adsorption is the molecular size of the solute, and on chitin it is the ability of the acetamido groups to act as ion exchangers.

The isotherms for certain dyes on cellulose are compared with that for Congo Red in Fig. 12, which illustrates the greater degree of adsorption which occurs as the size of the molecule increases.

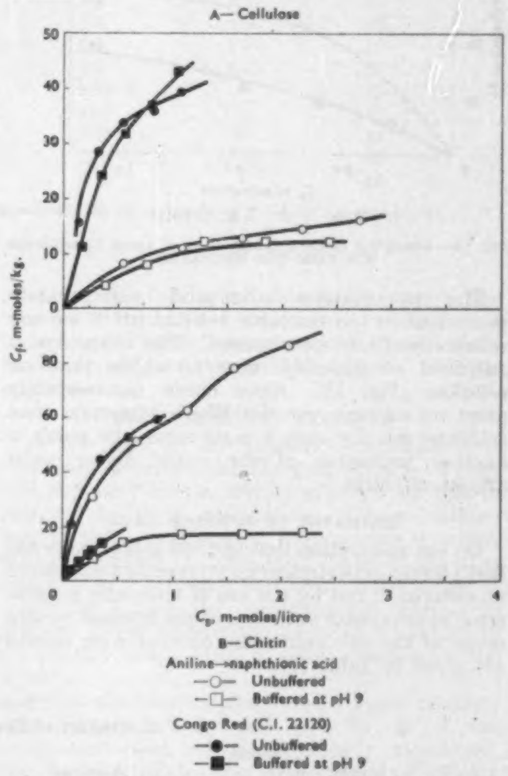


FIG. 11— Isotherms for Adsorption on Cellulose and Chitin from Aqueous Solutions at 50°C.

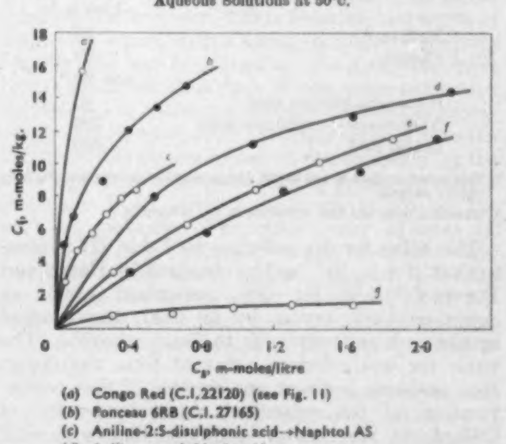


FIG. 12— Isotherms for Azo Compounds on Cellulose at 50°C.

SULPHATE ESTERS OF LEUCO VAT DYES

In order to examine the influence of very large multinuclear molecules, samples of the sulphate esters of the leuco compounds of flavanthrone and pyranthrone were examined.

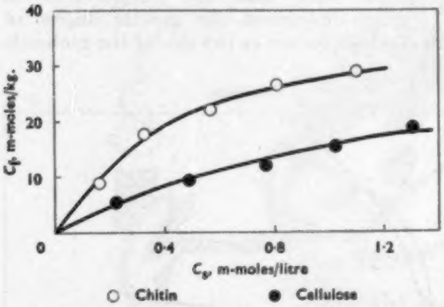


FIG. 13—Adsorption of the Sulphate Ester of Leuco Flavanthrone (C.I. 70601) from Water at pH 9

The pyranthrone compound unfortunately proved to be too insoluble even at pH 9 for any reliable result to be obtained. The other dye is adsorbed considerably more on chitin than on cellulose (Fig. 13). Since chitin can certainly exert no stronger van der Waals attraction than cellulose can for such a compound, the result is another indication of the much higher polar affinity of chitin.

ESTIMATES OF SURFACE AREA

On the assumption that the first inflection or the first plateau of the isotherms represents a completed monolayer [19], and by the use of molecular models, some approximate estimates of the internal surface areas of the two substrates covered with solutes are given in Table III.

TABLE III
Estimates of Surface Area at 50°C.

Solute Name	Assumed Cross-sectional Area (A.²)	Solvent	Surface Area (cm.²/g.) (approx.) Cellulose	Chitin
Methanol	20	Benzene	$5·5 \times 10^5$	$3·2 \times 10^5$
Phenol	25	*iso*Octane	—	53×10^5
	(ca. 60)*	Water	Nil	ca. 30×10^5*
Benzenesulphonic acid	40	Water	Nil	ca. 5×10^5†
Anthracene-1-sulphonic acid	100	Water	$3·3 \times 10^5$	ca. 13×10^5†
Congo Red	300	Water	$8·5 \times 10^5$	13×10^5

* This assumes that in *wet* chitin the acetamido groups are the only points of attachment, so that the adsorbed phenol molecules cannot be tightly packed.

† Measured from the first inflection in the isotherms.

The value for dry cellulose in Table III is close to that of 4×10^5 cm.²/g. obtained by Harris and Purves [cf. 13, p. 171] for dry mercerised ramie or cuprammonium rayon, by an analytical method involving treatment with thallous ethoxide. The value for wet cellulose obtained from the Congo Red isotherm is about one-quarter of that corresponding to the estimated saturation value of Cellophane regenerated cellulose film with C.I. Direct Blue 1 (at 90°C. in presence of 100 g. salt per litre)[13, p. 205].

Values obtained with large aromatic solute molecules in water are almost certainly too large, however, because some of the solute will be present as micelles and not as a molecularly dispersed monolayer.

AFFINITY MEASUREMENTS AND THEIR SIGNIFICANCE

SOURCE OF DYE AFFINITY FOR CELLULOSE

If the affinity of the anionic compounds is due entirely to van der Waals attraction between the cellulose molecular chains and the aromatic nuclei of the anions, then there should be a relation between the affinity and some parameter of the anions connected with their van der Waals attraction. Two such parameters have been considered here—

(i) The extinction coefficient ϵ for the absorbed band of longest wavelength. Peters and Sumner [20] found a linear relationship between the affinities for cellulose of a range of vat dyes and log ϵ. They argued that this identified van der Waals attraction as one source of the affinity, since Braude [21] had proved a relationship between the cross-sectional area of the π-electron system in a molecule, on which its van der Waals attraction for a surface may be expected to depend, and the logarithm of the extinction coefficient.

(ii) The logarithm of the length of conjugate chain of the dye molecule. The planar area of the molecule is not necessarily the best parameter to use in this comparison. The whole area of the dye molecule is probably not covered by cellulose chains, since these are rather widely separated from each other by their water layers. On the assumption that a uniform layer of water one molecule thick surrounds each cellulose chain, the repeat distance of parallel chains is ca. 13 A. It then appears from models that generally only one dye molecule can be accommodated by each chain with its water layer (Fig. 14). It seemed likely, therefore, that some function of the conjugate chain length of the dye molecule might offer a better means of comparison; the length of a planar dye molecule which can be oriented along one cellulose chain probably determines the magnitude of the physical attraction with which the π-electron system in the dye is held to the substrate. Consequently, affinity values were compared with the (logarithm of the) longest axis of the molecule, measured by the number of bonds counted from the extreme carbons of the aromatic nuclei or from the oxygen or nitrogen atoms (also halogens in some vat dyes,

TABLE IV

Affinity for Viscose Rayon, Extinction Coefficient (ε), and Length of Conjugate Chain of Sulphonated Dyes

Dye	C_s* (mM.)	C_f* (m-mole/kg.)	Affinity ($-\Delta\mu°$) (kcal./mole)	log ε	No. of Bonds in Chain
I	0·24	0·96	1·5	4·05	9
II	0·66	10·9	2·4	4·19	10
III	0·63	5·2	1·9	4·23	9
IV	0·45	7·8	2·4	4·29	11
V	0·35	9·8	2·8	4·43	13
VI	0·19	17·8	3·7	4·37	15
VII	0·33	119·0	5·7	4·49	21
C.I. 22311	—	—	6·5†	—	23
C.I. 22570	—	—	4·6†	—	19
C.I. 24410	—	—	7·7†	—	23
C.I. 24895	—	—	3·9†	—	23
C.I. 27720	—	—	4·8†	—	18

* Equilibrium concentrations in bath (C_s) and fibre (dry weight) (C_f) respectively. All baths contain 0·1 M-NaCl; 0·2 g. fibre in 10 c.c. solution; temperature 50°C.; time 6 hr.; rate of agitation 35 r.p.m.

† Values at 60°C. from Marshall and Peters [14] (NaCl concn. 0·01–0·02 N.). Other dyes non-linear; "length" values unreliable.

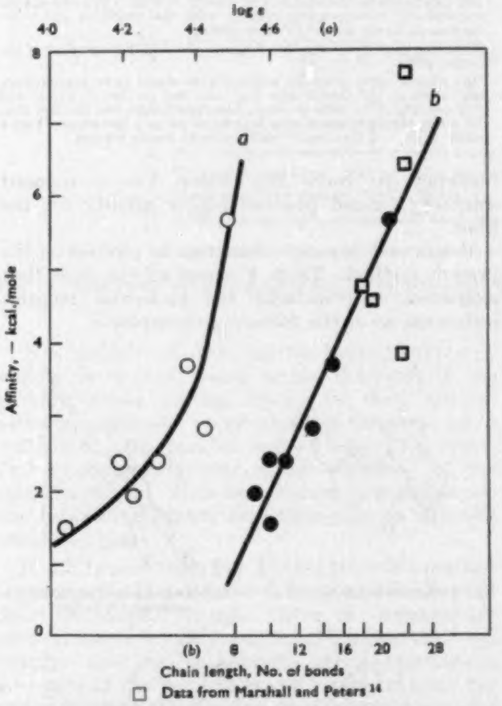


FIG. 14—Relationship between Affinity (at 50°C.) for Viscose Rayon of Sulphonated Azo Dyes and (a) Extinction Coefficient (logarithm) and (b) Length of Conjugate Chain

below) of terminal substituent OH, OR, NH_2, or NHR groups at either end of the axis.

Some data are quoted in Table IV, and Fig. 14 shows plots of affinity against both the above functions; the one based on molecular length is clearly the more linear plot.

This relationship, and the absence of any apparent correlation between the hydrogen-bonding capacity of the dyes* and their substantivity, suggest that the main, if not the only, source of affinity for cellulose in the dyes is the van der Waals attraction exerted between their molecules and the cellulose chains. Hydrogen-bond forces appear on this evidence to be of little importance.

* Cf. data in Fig. 12 with the number of potential bonding sites[8] in the dyes.

THE AFFINITY OF VAT DYES

In the light of the present conclusions it is necessary to re-examine the data given by Peters and Sumner [20] for the affinity of leuco vat dyes in relation to their constitution. These authors carried out an exhaustive investigation in which they determined the affinity of 73 leuco vat dyes and related compounds and compared changes in constitution with the corresponding changes in affinity. They studied the effect of alteration in the number and position of many groups upon the affinity.

Peters and Sumner also found a linear relationship between affinity and log ε for 16 of the compounds used, which, as already mentioned, they attributed to the dependence of affinity partly upon van der Waals attraction. This linear relationship, however, differs between two series of dyes. One series, with a nitrogen-containing group (mostly the amide group) in the molecule, have higher affinities than dyes of the same extinction coefficient but without a nitrogen-containing group. Peters and Sumner attributed this difference to the enhanced affinity conferred on the molecule by the ability of the nitrogen-containing groups to form a hydrogen bond with a hydroxy group in the cellulose molecule. The other series of dyes all consist of large aromatic nuclei with no substituents other than quinone groups. In the leuco state the latter would, of course, be in the ionised form ($-O^-$) and thus be rather unlikely to form hydrogen bonds with –OH groups in cellulose.

In one series of dyes, two anthraquinonylamide groups were separated by increasing numbers of $>CH_2$ groups (from 2 to 8), yet the affinity did not vary significantly (cf. Table V below). These authors conclude that, since clearly the water solubility of the dyes must steadily decrease with increase in their hydrophobic nature, affinity does

not depend on solubility, and it must have some more definite source. They then interpret their results on the hypothesis that this source lies in van der Waals attraction coupled with dipolar or hydrogen-bond forces.

The fact that quite large changes in water solubility produce no significant change in affinity may, however, be interpreted alternatively as the result of the dye remaining solvated by water even when adsorbed by the fibre. If the dye molecule left the water phase before associating with the fibre, as it would require to do for dye–fibre hydrogen bonds to be formed, then a greater

TABLE V

Affinity for Viscose Rayon (at 40°C.) (data of Peters and Sumner[20]) and Length of Conjugate Chain of Vat Dyes

Dye	Affinity $-\Delta\mu^\circ$ (kcal./mole)	No. of Bonds in Chain
*Anthraquinone	<1	7
1-Chloroanthraquinone	<1	7
1-Methylanthraquinone	<1	7
1-Methoxyanthraquinone	<1	7
1-Aminoanthraquinone (XII)	<1	7
2-Aminoanthraquinone	<1	7
*1-Acetamidoanthraquinone	1·52	9
2-Acetamidoanthraquinone	1·53	9
1-Chloroacetamidoanthraquinone	1·46	9
1-*N*-Methylaminoanthraquinone	1·46	8
1-*N*-Methylacetamidoanthraquinone	<1	7
1-Phenylacetamidoanthraquinone	<1	n.p.†
1-*op*-Dimethylphenylaminoanthraquinone	2·00	n.p.†
1:8-Diaminoanthraquinone	1·49	8
1:4-Diaminoanthraquinone	1·46	8
1:5-Diaminoanthraquinone	2·31	9
1:4-Bis-*N*-methylaminoanthraquinone	1·55	8
1-Benzylaminoanthraquinone	<1	7
*1-Benzamidoanthraquinone	2·37	11
2-Benzamidoanthraquinone	2·05	13
1-*β*-Naphthoamidoanthraquinone	3·61	12
1-Amino-4-benzamidoanthraquinone	2·94	11
1-Amino-5-benzamidoanthraquinone	2·39	11
1-Benzamido-4-methoxyanthraquinone	3·59	11
1-Benzamido-5-methoxyanthraquinone	3·50	12
1-*p*-Chlorobenzamido-5-methoxyanthraquinone	4·06	13
1-*o*-Chlorobenzamidoanthraquinone	1·98	n.p.†
1-*m*-Chlorobenzamidoanthraquinone	2·73	12
1-*p*-Chlorobenzamidoanthraquinone	3·02	12
1-*o*-Methylbenzamidoanthraquinone	2·07	n.p.†
1-*m*-Methylbenzamidoanthraquinone	2·74	11
1-*p*-Methylbenzamidoanthraquinone	2·68	11
1-*p*-Methoxybenzamidoanthraquinone	2·90	12
*1:4-Dibenzamidoanthraquinone	4·29	15 + 1‡
1:8-Dibenzamidoanthraquinone	ca. 2·60	? 11 + 1‡
1:4-Bis-*o*-chlorobenzamidoanthraquinone	3·42	n.p.†
1:4-Bis-*m*-chlorobenzamidoanthraquinone	4·98	15 + 1‡
1:4-Bis-*p*-chlorobenzamidoanthraquinone	5·20	17 + 1‡
1:4-Bis-*o*-methylbenzamidoanthraquinone	3·66	n.p.†
1:4-Bis-*m*-methylbenzamidoanthraquinone	4·56	15 + 1‡
1:4-Bis-*p*-methylbenzamidoanthraquinone	4·57	15 + 1‡
1:4-Bis-*p*-methoxybenzamidoanthraquinone	4·44	17 + 1‡
1:4-Bis-*o*-bromobenzamidoanthraquinone	3·54	n.p.†
1:4-Bis-*N*-methylbenzamidoanthraquinone	<1	7§
*1:5-Dibenzamidoanthraquinone	3·57	15
1:5-Bis-*o*-chlorobenzamidoanthraquinone	2·69	n.p.†
1:5-Bis-*m*-chlorobenzamidoanthraquinone	4·17	15
1:5-Bis-*p*-chlorobenzamidoanthraquinone	4·37	17
1:5-Bis-*o*-methylbenzamidoanthraquinone	2·71	n.p.†
1:5-Bis-*m*-methylbenzamidoanthraquinone	3·77	15
1:5-Bis-*p*-methylbenzamidoanthraquinone	3·73	15
1:5-Bis-*o*-methoxybenzamidoanthraquinone	2·39	n.p.†
1:5-Bis-*m*-methoxybenzamidoanthraquinone	3·86	15
1:5-Bis-*p*-methoxybenzamidoanthraquinone	4·11	17
Succinylbis-1-anthraquinonylamide	3·59	
Glutarylbis-1-anthraquinonylamide	3·63	
Adipylbis-1-anthraquinonylamide	3·64	
Pimelylbis-1-anthraquinonylamide	3·46	9 + 9
Suberylbis-1-anthraquinonylamide	3·46	
Azelaylbis-1-anthraquinonylamide	3·28	
Sebacylbis-1-anthraquinonylamide	3·53	

TABLE V—*continued*

Dye	Affinity $-\Delta\mu^\circ$ (kcal./mole)	No. of Bonds in Chain
**iso*Phthaloylbis-1-anthraquinonylamide	5·10	19
*1:4:5-Tribenzamidoanthraquinone	4·56	15 + 2
*Anthanthrone	3·53‖	9
*Dibenzanthrone	5·77	15
**iso*Dibenzanthrone	5·20	13
*1′:2′-Benzanthraquinone	1·01	9
*Pyranthrone	5·59	13
*1′:2′:6′:7′-Dibenzopyrene-7:14-quinone	4·35	11
3-Benzamido-2-naphthol	1·65	9
2-Hydroxy-3-naphthoanilide	1·88	10
3-Amino-2-naphthol	<1	6
3-Acetamido-2-naphthol	<1	7
Caledon Red BN (C.I. 68000)	4·70	13
*Indanthrone	ca. 6·60	15

* These compounds included in Fig. 2[20] and Fig. 16*a*.

† These compounds are so markedly non-planar that estimates of effective chain length are unreliable.

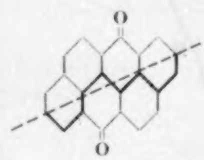
‡ The data for the 1:5-di- and the 1:4:5-tri-benzamidoanthraquinones show that the third substituent group increases the affinity a little. Models show that, when any one of the 1:4-dibenzamido compounds is aligned with its longest axis along one cellulose chain, the furthest end of the anthraquinone nucleus may lie over the adjacent chain. This has been allowed for in Table V by an arbitrary addition of one and two bonds to the length of all the 1:4 and the 1:4:5 compounds respectively, corresponding roughly with the length of dye overlapping on to the second cellulose chain.

§ Assuming that *N*-methylation destroys the conjugating effect of the amino group.

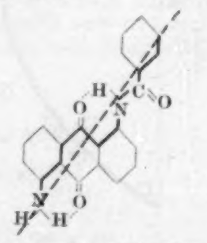
‖ The affinity value given for anthanthrone seems to be anomalously high both on the present plot (Fig. 15*a*) and on that of Peters and Sumner (Fig. 2[20]). Both its short molecular length and the fact that its substantivity is too low for it to be of use as a dye suggest that a value of ca. − 2 kcal./mole would be more nearly correct.

tendency to leave the water, i.e. a reduced solubility, would produce higher affinity for the fibre.

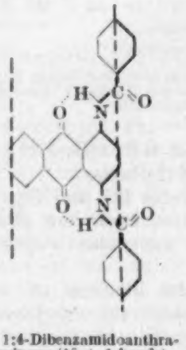
Peters and Sumner's data can be plotted on the present method. Table V shows all the dyes they examined, and includes the molecular lengths, estimated as in the following examples—



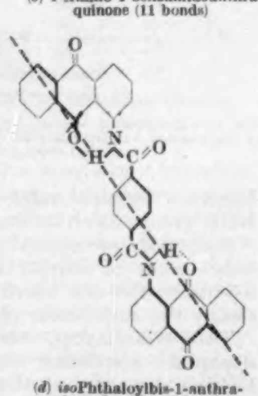
(*a*) Anthanthrone (9 bonds)



(*b*) 1-Amino-4-benzamidoanthraquinone (11 bonds)



(*c*) 1:4-Dibenzamidoanthraquinone (15 + 1 bonds)



(*d*) *iso*Phthaloylbis-1-anthraquinonylamide (19 bonds)

---- Suggested orientation of cellulose chain relative to dye molecule. The two lines in (*c*) show the possible orientation of adjacent cellulose chains, to illustrate the postulated overlap of the dye molecule.

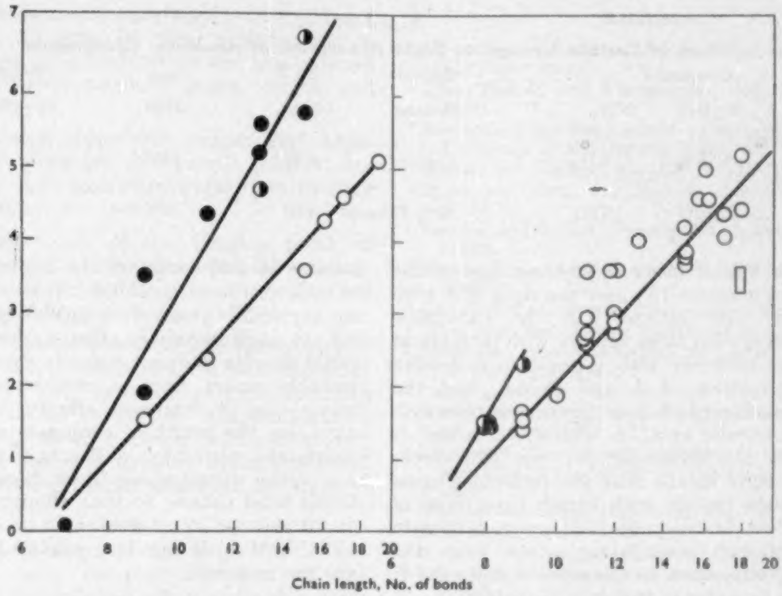


FIG. 15—Relationship between Affinity at 40°C. for Cuprammonium Rayon of Vat Dyes and Similar Compounds (data of Peters and Sumner[20]) and Length of Conjugate Chain

The models of the acylbis-1-anthraquinonylamides show that, owing to the flexibility of the paraffin chain joining them, the two anthraquinone nuclei can be arranged in the same plane with their axes parallel and at least 13 A. apart, i.e. approximately the repeat distance of the cellulose chains. Thus both halves of the molecule can be accommodated simultaneously on adjacent cellulose chains.

It will be seen from Fig. 15 that there is a marked tendency for the data to fall about two lines of different slope, though there is considerable scatter, which would be expected because the bond lengths can be considered only approximate measures of the van der Waals forces between dye and cellulose; they make no allowance e.g. for differences in conjugating power between terminal amino, bromo, chloro, or methoxy groups. (In this particular respect the extinction coefficient is a more precise parameter, though not, as already discussed, so accurate a measure of affinity.)

The dyes are now seen to be separated into (*a*) those in which the amido group forms part of the longest axis (these lie on the line of lower affinities), and (*b*) all other dyes, whether containing a hydrogen-bonding group or not*.

This means that, for a given length of planar molecule, the amido group is less effective than other groups in promoting affinity for cellulose. This indeed is to be expected if affinity is determined in a planar molecule solely by the length of the conjugate chain. The reason is that the amido group has only partial double-bond properties and thus is not an efficient conjugating group*. This can be seen clearly from the data in Table VI, which show that, when interposed between two benzene nuclei, this group is less effective in raising the extinction coefficient or the wavelength of maximum absorption than are the double-bond-containing azo and vinyl groups. The affinity of separate parts of a dye molecule which are not conjugated are approximately additive—cf. e.g. the value for 1-acetamidoanthraquinone (9 bonds, −1·52 kcal./mole) with that for its corresponding "double molecule", succinylbis-1-anthraquinonylamide (9 + 9 bonds, −3·59 kcal./mole). The slopes of the lines in Fig. 15 show that affinities of separate conjugated parts of a dye molecule are, however, much more than additive; i.e. the conjugation reinforces the attraction for cellulose, but, as just mentioned, less so in the amido dyes than in others because of the inefficient conjugation in their molecules.

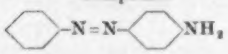
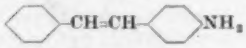
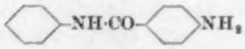
In Peters and Sumner's figure (affinity plotted against log ε) the condensed polynuclear quinones

* It is considered unlikely that the quinone group would in any case form a bond in the ionised leuco form, in which it exists during dyeing.

* The Stuart-type molecular models appear to show that the amide group introduces non-planarity, which could also account for the reduced affinity of the amido dyes—all the other dyes listed here are quite planar in these models—but this non-planarity is not evident in structures made from the Courtaulds models (cf. Fig. 2, reference [20]).

TABLE VI

Effect of Certain Groups on Light Absorption of Aromatic Compounds

Compound	Solvent	log ε	λ_{max}	Reference
	Hexane	4·46	3590	22
	Ethanol	4·38	3250	23
	95% Ethanol	4·00	2950	24

(Q) lie on a line of lower slope than that of the amidoanthraquinones (A) and the dyes (H) with heterocyclic >NH groups; i.e. the extinction coefficient of Q rises more rapidly with increase in affinity, and therefore with increase in molecular length, than those of A and H do. But the extinction coefficient of these planar dyes rises with the total molecular area, i.e. with width as well as length, and the difference between the slopes therefore simply means that the molecular areas of Q rise more rapidly with length than those of A and H. The heterocyclic >NH group is clearly a more efficient conjugating agent than the –CO·NH– group, since on the present plots the H dyes do not lie so far to the right as dyes A.

Summarising, the results of the present and of Peters and Sumner's investigations support the hypothesis that the adsorbed dye is attracted by van der Waals forces to the cellulose chain, which in aqueous solutions is surrounded by a layer of water molecules. The dye is held with its longest axis parallel to, and as closely as possible in contact with, the water–cellulose chain complex. The water layer probably prevents the dye approaching the cellulosic hydroxy groups closely enough for any cellulose–dye hydrogen bonds to form, and indeed the adsorbed dye may be considered to remain in the aqueous phase. The quinone groups in the polynuclear carbocyclic quinone dyes serve only as potential solubilising groups, and probably do not have any significant effect on affinity.

Technical Considerations

The following are some comments of possible technical interest, arising from the present conclusions—

(i) It seems likely that molecular structures for cellulose dyes— both direct and reactive— could be rapidly selected for synthesis and technical examination by constructing molecular models and estimating the probable affinity from the chain length.

(ii) High affinity for cellulose might be built up without degradation of hue by joining several small dye molecules in series by the $-CH_2{\cdot}CH_2-$ group. This group is an effective chromophoric block, but it also allows aromatic substituents at either end to be oriented with their axes parallel and in one plane.

(iii) It is usually supposed that an arylamido group in a dye or an intermediate is especially useful in conferring good affinity for cellulose, and in the past there has been some discussion upon the reason for the effect— whether it arises from an increase in conjugation of the dye molecule or in its hydrogen-bonding ability. It now appears that the arylamido group does indeed confer affinity, but not so effectively as other double-bond groups would do. Its technical value in dyes for cellulose probably arises from a combination of three causes— (*a*) it increases affinity by somewhat increasing the length of conjugate chain and yet maintaining planarity; (*b*) it acts at the same time as a partial chromophoric block, because of its low double-bond nature, so that affinity can be built up without too much deepening or dulling of the colour; and (*c*) it can very readily be introduced into the molecule.

Conclusion

MECHANISMS OF ADSORPTION OF SOLUTES BY CELLULOSE AND BY CHITIN

The following inferences may be drawn from this work—

(*a*) Cellulose can adsorb solutes by hydrogen bonding only in absence of water, whereas chitin can do so whether water is present or not.

(*b*) In water the cellulose molecules are protected against hydrogen-bonding of solutes in dilute solution* by a firmly bound layer of water molecules, and only solutes whose molecules have high attraction for cellulose can be adsorbed. There is a little evidence that high attraction depends upon the presence of a strongly ionised group in the solute molecule. If this is so, it suggests that this group assists substantivity by enabling the solute molecule to be better dissolved in the water surrounding the cellulose [cf. 18].

(*c*) Solvated water appears to prevent intermolecular hydrogen bonding by hydroxy groups in carbohydrates and derivatives, but not in simple alcohols.

(*d*) In water chitin can form hydrogen bonds with some solutes and can also take part in ion-exchange reactions, in both cases through its acetamido group. Its glucosidic hydroxy groups appear to be protected by water in the same way as those of cellulose. Its molecular chains do exert van der Waals attraction for adsorbing solutes in much the same way as those of cellulose, but the attraction appears to be weaker.

The following additional facts support these suggestions—

(i) For high cellulose substantivity, dyes must have planar molecules and long conjugate systems[27].

* From concentrated solutions hydrogen-bond adsorption may occur; e.g. urea [28].

(ii) The same requirements apply to arylides of the Naphtol AS type, for their substantivity is said to depend upon chelation of the amide group with the adjacent phenolic group, which will ensure planarity [28].

(iii) Monolayer experiments suggest that simple carbohydrate molecules in aqueous solution are prevented by their associated water from forming hydrogen bonds with dyes [29].

(iv) Determination of the freezing point of moisture in cellulosic fibres shows that the cellulose chains in the non-crystalline parts of the fibre are in a state resembling solution in water [30].

(v) Rate measurements of the alcoholysis of cellulose are said to demonstrate a multimolecular layer of water at the cellulose–liquid interface which acts as a barrier in high-temperature reactions. Only at high concentrations of alcohol is the layer appreciably modified and transformed into a less effective barrier of alcohol molecules [31].

NOTE

Since the submission of this paper Lead [32] has published a note drawing attention to the possibility of the cellulose affinity of a dye being derived from a form of hydrogen bond with its π-electron system.

* * *

The authors thank Professor P. D. Ritchie for his interest and encouragement, Messrs. Courtaulds Ltd. for supplying viscose rayon, Dr. A. C. Robson and Imperial Chemical Industries Ltd., Dyestuffs Division, for preparing the samples of sulphuric esters of leuco vat dyes, and Dr. M. A. T. Rogers and Imperial Chemical Industries Ltd., Dyestuffs Division, for supplying several other solutes. The carapaces of *Nephrops norvegicus* were obtained from the Marine Biological Research Laboratory, Millport, Isle of Cumbrae.

COLOUR CHEMISTRY RESEARCH LABORATORY
DEPARTMENT OF TECHNICAL CHEMISTRY
ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY
GLASGOW C.1

(*Received 21st May 1957*)

References

1 Giles, Hassan, Laidlaw, and Subramanian, J.S.D.C., **74**, 647 (Sept. 1958).
2 Giles, Hassan, and Subramanian, *ibid.*, **74**, 682 (Oct. 1958).
3 Richards, *The Integument of Arthropods* (Minneapolis: University of Minneapolis, 1950).
4 Knecht and Hibbert, J.S.D.C., **42**, 343 (1926).
5 Meyer and Mark, *Ber. deutsch. chem. Ges.*, **61**, 1936 (1928).
6 Darmon and Rudall, *Faraday Soc. Discussions*, (9), 251 (1950).
7 Arshid, Giles, and Jain, *J.C.S.*, (*a*) 559 (1956); (*b*) 1272 (1956).
8 Campbell, Cathcart, and Giles, J.S.D.C., **73**, 546 (1957).
9 Giles, Jain, and Hassan, *Chem. and Ind.*, 629 (1955).
10 Hackman, *Australian J. Biol. Sci.*, **8**, 83, 530 (1955).
11 Thor, *USP* 2,168,374.
12 Clunie and Giles, *Chem. and Ind.*, 481 (1957); Arshid, Desai, Duff, Giles, Jain, and Macneal, J.S.D.C., **70**, 399 (1954).
13 Vickerstaff, *The Physical Chemistry of Dyeing* (London and Edinburgh: Oliver & Boyd Ltd. 2nd edition 1954).
14 Marshall and Peters, J.S.D.C., **63**, 446 (1947).
15 Flett, *ibid.*, **68**, 59 (1952).
16 Marsden and Urquhart, *J. Textile Inst.*, **33**, T 105 (1942).
17 Giles, Mehta, Stewart, and Subramanian, *J.C.S.*, 4360 (1954).
18 Derbyshire and Peters, J.S.D.C., **71**, 530 (1955).
19 Brunauer, *The Adsorption of Gases and Vapours* (London: Oxford University Press. 1944), p. 287.
20 Peters and Sumner, J.S.D.C., **71**, 130 (1955).
21 Braude, *J.C.S.*, 379 (1950).
22 Burawoy, *ibid.*, 1865 (1937).
23 Bergmann and Fischer, *ibid.*, 2837 (1953).
24 Grammaticakis, *Bull. Soc. chim.*, **18**, 534 (1951).
25 Robinson, *Faraday Soc. Discussions*, (16), 125 (1954).
26 Preston, Clark, Beath, and Nimkar, *J. Textile Inst.*, **45**, T 504 (1954).
27 (*a*) Hodgson, J.S.D.C., **49**, 213 (1933); (*b*) Hodgson and Marsden, *ibid.*, **60**, 210 (1944).
28 Delépine, *Compt. rend. Acad. Sci. Paris;* **237**, 69 (1953): through J.S.D.C., **71**, 56 (1955).
29 Allingham, Giles, and Neustädter, *Faraday Soc. Discussions*, (16), 92 (1954).
30 Preston and Nimkar, *Text. Research J.*, **23**, 119 (1953).
31 Sharkov, Korol'kov, and Krupnova, *J. Appl. Chem. U.S.S.R.*, **27**, 319 (1954): through J.S.D.C., **70**, 324 (1954).
32 Lead, J.S.D.C., **73**, 464 (1957).

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Covalently Bound Azo Dyes

In view of the interest aroused by the recent introduction of reactive dyes for cellulose [1], some notes on a method of obtaining insoluble azo dyes which are covalently bound to cellulose may be of interest to readers of this *Journal*. This method, which was described before the commercial reactive dyes were introduced [2, 3], depends upon prior preparation of "ω-cellulose" with degrees of substitution up to 0·3 by reaction between soda-cellulose and ω-chloro-p-aminoacetophenone $Cl{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}NH_2$. The product is a cellulose ether containing an aromatic amino group, which can be diazotised and coupled in the usual way to produce azo dyes which are covalently bound to the substrate. The raw cellulose derivative can also be xanthated, either before or after diazotisation and coupling, and subsequently spun into fibres in the usual manner. The fibres spun from uncoupled material may themselves be diazotised and coupled.

The coloured materials have very high fastness to soaping treatments, and their light fastness also is good (Giles, personal communication). It seems likely that the high light fastness may be due partly to the substituted dye forming an integral part of the cellulose micelles, and partly to association of the aromatic portions of the dye. Warwicker [4] has shown that the nuclei of basic dyes adsorbed on acidic oxycelluloses can associate, even though their points of attachment to the surface may be widely separated. For this

to occur, slight buckling of the substrate polymer chains probably must occur: thus the intermolecular associative forces of the dye molecule can overcome the resistance of the polymer chain to deformation.

R. R. McLaughlin

Department of Chemical Engineering
and Applied Chemistry
University of Toronto
Toronto 5
Canada

29th September 1958

[1] Cf. e.g. Vickerstaff, T., J.S.D.C., **73**, 237 (1957).
[2] McLaughlin, R. R., and Mutton, D. B., *Canadian J. Chem.*, **33**, 646 (1955).
[3] Idem, *USP* 2,727,034; *Canadian Patent* 524,927.
[4] Warwicker, J. O., *J. Textile Inst.*, **49**, T 148 (March 1958).

Paper Chromatography of Disperse Dyes

A method has been described by Elliott and Telesz [1] for the separation and identification of disperse dyes. Unmodified Whatman paper No. 3MM and petroleum ether (boiling range 65–70°C.) saturated with 98% methanol as eluant were used. The authors were aware that this particular combination had certain limitations, particularly "when the R_f values of two or more dyes are close together or when a component streaks badly". Subsequently Janoušek [2] reported his use of acetylated paper and chlorobenzene as eluant, and in an earlier publication Harris and Lindley [3] had used paper impregnated with a 1% solution of secondary cellulose acetate in acetone, butyl acetate–pyridine–water (1 : 5 : 10) being the eluant.

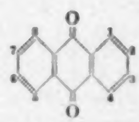
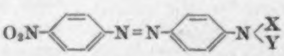
We have now found that, after slight modification, the procedure used by Franc [4] for the separation of aromatic nitro compounds is admirably suited to the paper chromatography of disperse dyes: Whatman paper No. 4 is impregnated with petroleum distillate (Shell, boiling range 190–275°C.) by dipping first in solvent only, then in a mixture of benzene and distillate (9 : 1), and drying in air. A 0·25% solution of the dye in acetone is spotted on the paper, and the chromatogram is eluted with an ethanol–water–acetic acid (20 : 14 : 1) mixture.

Some representative R_f values of selected disperse dyes are shown in Table I. All chromatograms were run by the descending technique, at 21 ± 1°C.

In Method A[1], Whatman No. 1 paper was used, eluted for 3 hr., the starting line–solvent front distance D being 26 cm. In method B, Whatman No. 4 paper, pretreated as described above, was used, eluted for 9 hr., D = 25 cm.

Table I

Representative R_f Values of Selected Disperse Dyes

Code No.	*Colour Index* No.	Chemical Constitution	R_f Values Method A[1]	R_f Values Method B
	Anthraquinonoid Dyes			
AM 1	C.I. Disperse Orange 11	1-NH_2, 2-CH_3	0·69[c]	0·62[c]
AM 2	C.I. Disperse Red 15	1-NH_2, 4-OH	0·30[b,c]	0·65[c]
AM 3	C.I. Disperse Blue 22	1-NH·CH_3, 4-OH[a]	0	0·58
		1:4-Di-NH·CH_3	0·01	0·75
			0·71	0·80
AM 5	C.I. Disperse Red 4	1-NH_2, 2-O·CH_3, 4-OH	0·54[b,c]	0·51[c]
AM 7	C.I. Disperse Violet 1	1:4-Di-NH_2	0·01	0·77
AM 8	C.I. Disperse Violet 4	1-NH_2, 4-NH·CH_3	0·13	0·75
AM 9	C.I. Disperse Blue 19	1-NH_2, 4-NH·C_6H_5	0·57	0·59
AM 13	C.I. Disperse Blue 14	1:4-Di-NH·CH_3	0·70	0·57
AM 15	C.I. Disperse Blue 24	1-NH·CH_3, 4-NH·C_6H_5	0·78	0·24
AM 20	C.I. Disperse Red 11	1:4-Di-NH_2, 2-O·CH_3	0·01[c]	0·65[c]
AM 21	C.I. Disperse Violet 8	1:4-Di-NH_2, 5-NO_2	0	0·72
AM 24	C.I. Disperse Blue 1	1:4:5:8-Tetra-NH_2	0	—[d]
	Azo Dyes			
AZ 2	C.I. Disperse Orange 3	X = Y = H	0	0·01
			0·15	0·64
AZ 10	C.I. Disperse Red 1	X = C_2H_5, Y = CH_2·CH_2OH	0	0·09
			0·05[a]	0·21
			0·80[e]	0·79[a]
AZ 12	C.I. Disperse Red 19	X = Y = CH_2·CH_2OH	0	0·79
AZ 19	C.I. Disperse Orange 1	X = H, Y = C_6H_5	0·49	0·41

Notes—
(*a*) Main component
(*b*) Appreciable tailing
(*c*) Fluorescence of spots under ultraviolet radiation—
AM 1 Yellowish pink
AM 2 Reddish purple
AM 5 Yellowish pink
AM 20 Pink
(*d*) R_f value uncertain because of bad tailing
(*e*) Spot hardly visible in ordinary light but detectable under ultraviolet radiation.

The above procedure may be termed "reverse-phase" chromatography with respect to the method used by Elliott and Telesz [1]. Here we have a non-polar stationary phase and a polar eluant (mobile phase), whereas in the former case the conditions were reversed.

In our view the two methods are complementary. Certain dyes, e.g. C.I. Disperse Violet 8 (AM 21) and C.I. Disperse Red 19 (AZ 12) both had $R_f = 0$ by method A[1], and by method B their R_f values are 0·72 and 0·79 respectively. It is of interest to note that C.I. Disperse Red 1 (AZ 10), which is represented in the *Colour Index* as a single entity, appears, in fact, to be a three-component mixture. In the case of C.I. Disperse Blue 22 (AM 3) the formulae of two components are given, but this dye also appears to be a three-component mixture.

We intend to publish a comprehensive account of the chromatographic behaviour of disperse dyes as a class, and it is hoped that this investigation (which is now in progress) will also yield information on the correspondence between R_f values and chemical constitution of dyes. It may be of general interest to report that the application of the above method to the separation and identification of polynitronaphthalenes arising from the further nitration of mono-, di-, and tri-nitronaphthalenes met with some success.

C. D. JOHNSON
L. A. TELESZ

SCHOOL OF CHEMISTRY
COLLEGE OF TECHNOLOGY AND COMMERCE
LEICESTER

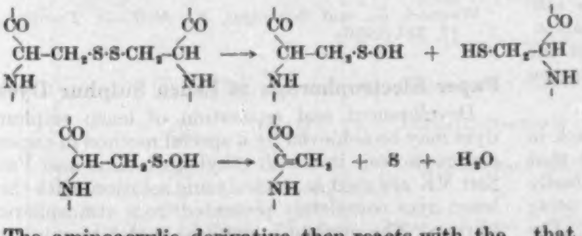
2nd October 1958

[1] Elliott, K., and Telesz, L. A., J.S.D.C., 73, 8 (1957).
[2] Janoušek, J., *ibid.*, 73, 328 (1957).
[3] Harris, P., and Lindley, F. W., *Chem. and Ind.*, 922 (1956).
[4] Franc, J., *Chem. Listy*, 49, 873 (1955).

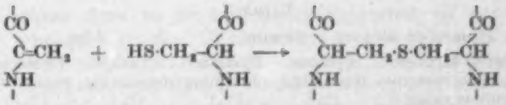
A Suggested New Mechanism for the Degradation of Cystine in Alkaline Solution

The mechanism of the reaction between cystine and alkaline solutions has been intensively studied. Speakman and Whewell [1] suggested that the cystine is converted into lanthionine, and this was later confirmed by the isolation of lanthionine from an alkali-treated wool [2]. Two mechanisms have been postulated for this reaction—

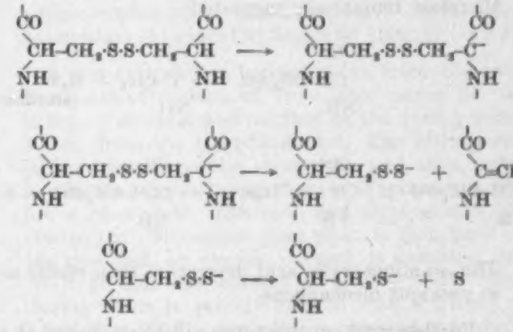
Speakman [3] and Schöberl [4] suggested that the disulphide bond hydrolyses with the formation of an unstable sulphenic acid, which decomposes to give an aminoacrylic derivative—



The aminoacrylic derivative then reacts with the cysteine to form lanthionine—



The second mechanism, suggested by Mizell and Harris [5] and modified by Rosenthal and Oster [6], postulates the ionisation of an α-hydrogen atom from the cystine residue, leaving a carbanion which decomposes to give an unstable disulphide ion and the aminoacrylic derivative previously postulated—



Swan [7] has shown that $\alpha\alpha'$-dimethylcystine is considerably more stable to alkali than is cystine, and suggests that the α-hydrogen atom is essential to the reaction, concluding that the second mechanism is more probable.

Recent work in these laboratories on the reaction between ethylamine and wool indicates that the cysteine residues play an important part in the decomposition of cystine residues. Accordingly studies were undertaken on the influence of free cysteine on the decomposition of free cystine in boiling molar ethylamine solution.

Samples of cystine and cysteine were dissolved in ethylamine and boiled for differing periods of time. Cystine and cysteine analyses were carried out colorimetrically on the various solutions before and after treatment (hydrogen sulphide being removed before estimation). Table I gives some of the results obtained. It can be seen that under these conditions cystine is relatively stable in boiling ethylamine, but cysteine is decomposed to a considerable extent after 3 hr.

Analyses of mixtures after treatment show a surprising increase in cysteine content accompanied by an appreciable decrease in the cystine content.

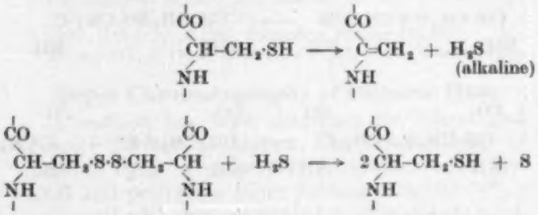
In all cases where cystine and/or cysteine are destroyed the solution has the characteristic yellow colour of alkaline polysulphide, and hydrogen sulphide can be evolved on acidification with the accompanying precipitation of sulphur. A chromatographic examination of the resulting solutions showed lanthionine to be among the products of the reaction.

From these observations it appears that cysteine plays a major rôle in the decomposition of cystine in alkaline solution, and that one stage in the reaction is the reduction of cystine to cysteine.

TABLE I

Time of treatment	30 min.		3 hr.	
Initial Mixture (cystine/cysteine molar ratio)	Cystine remaining (%)	Cysteine remaining (%)	Cystine remaining (%)	Cysteine remaining (%)
Cystine only	100	—	95·4	—
Cysteine only	—	96·4	—	46·4
34·8	75·0	1025·5	—	—
1·4	70·2	145·7	—	—
14·9	—	—	28·3	1437·0
0·89	—	—	45·3	122·9

The following mechanism for the reaction is therefore tentatively suggested—



The α-aminoacrylic acid derivative then reacts as in previous mechanisms.

Further work on this topic will be published at a later date.

We wish to thank the Bradford City Council for a grant to one of us (M.A.H.).

R. L. ELLIOTT
R. S. ASQUITH
M. A. HOBSON

DEPARTMENT OF CHEMISTRY AND DYEING
INSTITUTE OF TECHNOLOGY
BRADFORD 7
YORKSHIRE

17th October 1958

[1] Speakman and Whewell, J.S.D.C., **52**, 380 (1936).
[2] Horn, Jones, and Ringel, *J. Biol. Chem.*, **138**, 141 (1941).
[3] Speakman, *Nature*, **132**, 930 (1933).
[4] Schöberl, *Annalen*, **507**, 111 (1933).
[5] Mizell and Harris, *Bur. Stand. J. Res.*, **30**, 48 (1943).
[6] Rosenthal and Oster, *J. Soc. Cosmetic Chemists*, **5**, 286 (1954).
[7] Swan, *Nature*, **179**, 965 (1957).

Bleaching with Peroxide

In their very interesting paper on bleaching with hydrogen peroxide Chesner and Woodford[1] discuss the rôle of natural impurities found in grey cotton. According to their findings, protein has "in fact, been found advantageous in producing greater stability of the liquor". Further, they prove that the incorporation of proteins is also useful in the presence of copper contamination. This would mean that proteins can prevent the strongly catalytic action of copper on hydrogen peroxide solutions.

These findings are not completely new. Back in 1936 G. Wiegand and K. Schöniger found that pigmented cuprammonium rayon is badly damaged by the normal bleaching method using silicate-stabilised alkaline peroxide solutions. The addition of degraded polypeptides was found useful, but "the condensation products derived from the action of fatty acids on degraded proteins showed especially advantageous properties". The commercial product used for their investigations was Lamepon A (Chemische Fabrik Grünau AG.). That would mean, if these findings are correct, that the presence of such a condensation product in the bleaching liquor gives a still higher margin of safety than the natural impurities brought in by grey cotton.

KARLHEINZ WEIBLE

REUTLINGEN-BETZINGEN
KRONENGASSE 5
GERMANY

22nd September 1958

I am grateful to Herr Weible for having drawn my attention to the work carried out on regenerated cellulose by Wiegand and Schöniger.

All the experiments which have been carried out to date support the fact that the incorporation in a silicate-stabilised liquor of a wide range of soluble proteins and degraded polypeptides enhances the safety margin of the bleaching process, and also results in a net saving in the chemical cost of hydrogen peroxide consumed.

The reason for this apparent sequestering property in the case of copper is, no doubt, associated with the behaviour of one or more of the nitrogen atoms in the protein or peptide, possibly in the amino or imino form. Further work is being carried out in an attempt to elucidate this point.

It is difficult to make a comparison between the stabilising influence and margin of safety imparted by the natural impurities in cotton, on the one hand, and proteins and degraded polypeptides on the other. The former may vary widely depending on the source of the cotton, whilst the quantities of the latter, whose action is more specific for copper, may be adjusted. It would therefore be more correct to state that their addition enhances the margin of safety, which is complementary to that provided by the impurities in the grey cotton. No doubt the same type of consideration would apply to the product Lamepon A.

L. CHESNER

LAPORTE CHEMICALS LTD.
P.O. BOX 8
LUTON
BEDFORDSHIRE

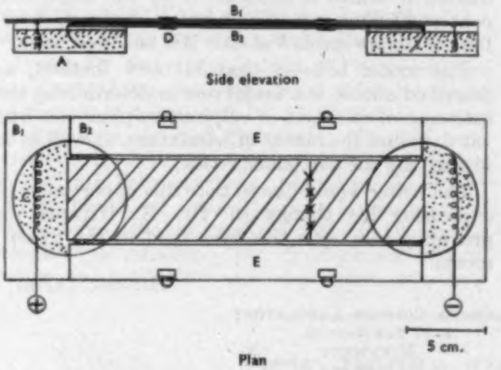
14th November 1958

[1] Chesner, L., and Woodford, G. C., J.S.D.C., **74**, 531 (July 1958).
[2] Wiegand, G., and Schöniger, K., *Melliand Textilber.*, **17**, 337 (1936).

Paper Electrophoresis of Leuco Sulphur Dyes

Development and separation of leuco sulphur dyes may be achieved by a special method of paper electrophoresis in which ethylenediamine and Vat Salt MK are used as electrolysing solution, with the leuco dyes completely protected from atmospheric oxygen. The method is applicable also to sulphur vat and vat dyes.

Sulphur dyes are produced on a large scale, as they are cheap and very useful for dyeing cotton, but the resulting colours are not too bright. Each dye is considered to be a mixture, and quite a few of them have their chemical structures still undetermined.



A Dish
B_1, B_2 Two glass plates holding the filter paper between them
C Platinum electrode
D Clips (four) fixing the glass plates
E Dry filter paper to absorb excess liquid oozing from between the glass plates during the course of electrophoresis. This dry filter paper is placed 2 mm. from each side of the central filter paper and parallel to it.

FIG. 1— Apparatus for Electrophoresis of Leuco Dyes

Some sulphur dyes are soluble in bases, but most of them are normally insoluble. However, on reduction to the leuco form, these dyes become soluble in bases. Unfortunately, their affinity for cellulose and their tendency to re-oxidation are then so great that it is practically impossible for these dyes to be effectively subjected to paper chromatography. If the individual components of such sulphur dyes could be determined by some simple means, then it would go a long way toward clarifying the nature of these types of dyes.

The transverse line in the centre of Fig. 1 indicates filter paper for conducting electricity, a × thereon showing the original dyeing point where a leuco dye is to be marked. Dotted parts indicate electrolyte.

The electrolysing solution was 85% ethylenediamine–concentrated ammonium hydroxide–ammonium chloride–Vat Salt MK* (100 : 25 : 1 : 1·5).

A line is drawn at a point 3 cm. from the left-hand end of a sheet of Toyo filter paper No. 50 (5 cm. × 28 cm.), and another at the dyeing point 10 cm. from the right-hand end. The filter paper is first dipped in the electrolyte and then, after having its surplus liquid shaken off, placed on the lower glass plate, with each end dipping into the electrolyte. The upper glass plate is then fixed in position and an electric current is switched on. After 20 min. the current is switched off. The dyeing point is quickly marked with a 2 mm. × 4 mm. spot of 0·1% dye solution prepared separately by dissolving the dye in the same electrolyte. The upper glass plate is then fixed with the clips, and the current is switched on again. The dye mark will be seen to move with leuco dyes.

The conditions are— 370 v. D.C./22 cm., 22 ma./5 cm., 4 hr.

As will clearly be seen from Fig. 2, sulphur dyes are mostly mixtures of dyes of similar hue, and the extent of admixture varies greatly from dye to dye. The colour is rather dull before separation, but that of each spot formed after separation is fairly clear.

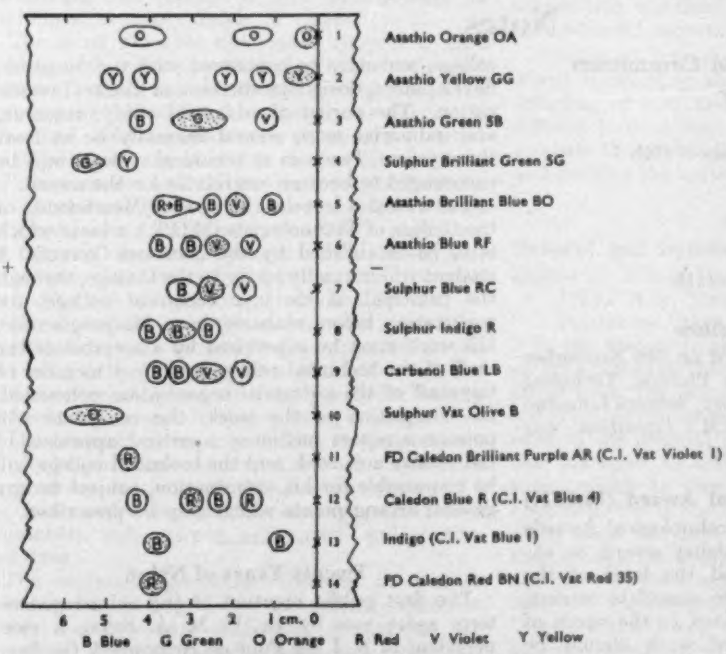


FIG. 2— Electrophorograms of Sulphur, Sulphur Vat, and Vat Dyes (dotted spots indicate main dye components)

Ordinary paper chromatography has been tried on sulphur dyes by means of such bases as pyridine, monoethanolamine, and ethylenediamine at different concentrations with or without the addition of butanol. In dilute bases no good development of colours has been observed, while in concentrated bases development reaches as high as $R_f = 1$ accompanied by extreme tailing. Such tailing does not vanish even when the R_f value is brought down by addition of butanol, and only very little separation is seen. No better results are obtained by making any of the above bases the electrolysing solution.

* Thiourea dioxide (C.I. Reducing Agent 11).

Even when sulphur dyes, after being reduced to the leuco form by addition to the developing solution of a reducing agent, are developed in nitrogen gas or in a cylinder filled with liquid paraffin, separation is prevented by the oxidation of dyes which necessarily takes place in the course of colour-spot movement, since complete elimination of oxygen is not possible by such means.

Only by means of the apparatus shown in Fig. 1 can air be completely excluded, thereby allowing dyes to migrate in the leuco form and to show themselves in their respective colours the moment they are exposed to the air. Thus the results of dye separation can be clearly observed.

The only electrolyte that can meet the purpose is the above-mentioned liquid consisting mainly of ethylenediamine, which itself acts as the reducing agent.

Since the substantivity of leuco dyes for the cellulose of filter paper cannot be prevented by bases of low concentration, extremely high concentrations must be used. An addition of concentrated ammonia to such bases will make the latter more effective.

Some rise of temperature registered in the course of electrophoresis is believed to be helpful in reducing dyes and keeping them in the reduced form.

Ammonium thioglycollate has proved unsuitable as a reducing agent, since it is easily destroyed by oxidation, which is accelerated by the slight iron content of filter paper or of water. Instead, therefore, the more stable Vat Salt MK has been used.

The writer believes that his new method, as described above, is a useful one in determining the existence of mixtures in sulphur, sulphur vat, and vat dyes and the extent of admixture, as well as in identifying the component dyes.

The writer would like to take this opportunity of expressing his thanks to Dr. H. Hiyama for providing him with the dyes used in the experiments.

Hiromi Tajiri

Osaka Customs Laboratory
4-55 Sanjo-dori
Minato-ku
Osaka
Japan

28th July 1958

ERRATUM

Rendering Wool Fabrics dimensionally stable to Repeated Washing. Rohm & Haas Co. *BP* 801,987 (J.S.D.C., **74**, 808 (Nov. 1958))— The proportion of 4-vinylpyridine in the copolymer should be **3–15%** (not "3·15%"), and the temperature should be **not below** 100°C.

Notes

Meetings of Council and Committees November

Council— 5th

Finance and General Purposes— 19th

Publications— 18th

Examinations Board— 26th

Society's Medals— 19th

Review of Textile Progress— 11th

Election of Fellow

At a meeting of Council held on 5th November 1958, James Norman Fulton Phillips, Technical Director and Head of Laboratory, Señores Lonalino S.A., San Martin, F.C.N.G.B.M., Argentina, was elected a Fellow of the Society.

A New Higher Technological Award (M.C.T.)

The National Council for Technological Awards propose to create a single higher award to encourage further study beyond the level of the Diploma in Technology and to stimulate original investigation of problems related to the needs of industry. The programme of work should be carried out jointly in industry and at a technical college, and may be concerned with e.g. research, development, design, production, or market investigation. The period of advanced study, research, and industrial work should normally be at least three years. Teachers in technical colleges will be encouraged to become candidates for the award.

The award is to take the form of Membership of the College of Technologists (M.C.T.), a body which is to be established by the National Council. A student will normally apply to the College, through the principal of his own technical college, for registration before embarking on his programme. His work must be supervised by a member of the staff of the technical college and by a member of the staff of the industrial organisation concerned. On completion of the work, the candidate will present a report including a critical appraisal of the results achieved, and the technical college will be responsible for his examination, subject to any general arrangements which may be prescribed.

Twenty Years of Nylon

The first public mention of the coined generic term *nylon* was by Dr. C. M. A. Stine, a vice-president of E. I. du Pont de Nemours & Co. Inc., at the New York *Herald Tribune's* eighth annual

Forum on Current Problems on 27th October 1938. Three months earlier the *Daily News Record* had secured a scoop with an account of "Fiber 66", the laboratory designation. Nylon had then been introduced in toothbrush bristles, fishing lines were marketed a few months later, and nylon stockings were first shown publicly in February 1939 at the San Francisco World's Fair, but not offered for sale throughout the U.S.A. until May 1940.

It was Dr. Stine who in 1927 had conceived the fundamental research programme which led to the production of nylon, and Dr. W. H. Carothers was brought from Harvard University. The first truly synthetic fibre was produced in 1930, and "Fiber 66" on 28th February 1935. Among problems that had to be solved before large-scale manufacture was possible were the production of adipic acid and hexamethylenediamine, the development of new pumps, a new alloy for the spinnerets, new winding machinery, and, almost at the last moment, a new method of sizing.

Review of Textile Progress

The *Review* will reach its tenth volume in 1959, and the joint committee of the Society and the Textile Institute which is responsible for its production feels that Volume 11 will provide a suitable opportunity for the introduction of any changes in style and presentation which may appear desirable in the light of experience of the earlier volumes. The committee considers that members of the two bodies and non-members who use the *Review* may well have valuable suggestions to make, and they are invited to send any comments either to the Editor, Society of Dyers and Colourists, 19 Piccadilly, Bradford 1, Yorkshire, or to the General Secretary, Textile Institute, 10 Blackfriars Street, Manchester 3.

New Books and Publications

Hydrogen Ions
Their Determination and Importance in Pure and Industrial Chemistry
Volume Two

By H. T. S. Britton. 4th edition 1956. Pp. xix + 489. London: Chapman & Hall Ltd. Price, 70s. 0d.

This second volume is concerned mainly with the *importance* of pH values in pure and industrial chemistry, the first volume being about methods of determination (cf. J.S.D.C., **74**, 45 (Jan. 1958)). Its appeal is likely to be greatest to teachers, who need arguments to justify spending so much time inculcating the concept of pH, by stressing its usefulness in many fields of chemistry.

The most valuable theoretical chapter is that dealing with redox potentials, but in the reviewer's opinion it would have been more appropriate in the first volume. Titration in non-aqueous solvents is described, and methods are outlined for determining the amount of acid in shellac, oils and fats, cellulose nitrate and acetate (in methylcellosolve), the titration of leuco vat dyes, weak organic bases (in glacial acetic acid) and weak acids (in a mixture of benzene and *iso*propanol). Other analytical techniques involving precipitation or complex formation are also thoroughly dealt with.

The industrial applications to soils, ceramics, ore-flotation, and the electrodeposition of metals will not greatly interest readers of this *Journal*, nor will the five chapters on dairy products, baking and brewing, except in their private capacity!

The remaining chapters outline the importance of hydrogen ion concentration in industries covered by sections of the *Journal* abstracts— e.g. water and sewage; leather tannage (chrome and vegetable); pulp, paper, and sugar; and textiles and dyes.

The author's particular interest in leather chemistry is betrayed by the minute detail in which the processes of leather production are described, which, though interesting, are not strictly relevant to the main topic of the book.

In the chapter on textiles and dyes, of which it is possible to make a more rigorous assessment, it is found that the references are quaint and old-fashioned. While there is a group of five from 1922 to 1938, there are only 21 after 1942, the most recent being 1951, and these are only patents.

The last 17 pages are devoted to miscellaneous items on sweets, canning of fruit, jam, meat, insulin, photography, dentifrices, antiseptics, tobacco, explosives, and fire extinguisher foams, but there is an occasional reference worth having on insulin, lead chromate pigments, emulsions, soap, rubber latex, plastics, crystallising non-caking ammonium sulphate, scrubbing boiler flue gases, and colloidal carbon.

Finally, if minor criticism be permitted, it is worth mentioning that the typography, with its mingling of text and formulae, makes the book difficult to read, and only the authoritative scope compels the reader to persist in reading the book and justifies the reviewer in recommending it.

L. Peters

Natural and Synthetic Fibers Yearbook 1957

Edited by Milton Harris and H. Mark. Pp. iii + 1144. New York and London: Interscience Publishers. 1958. Price, $45.00.

In the preface to this large volume it is claimed as an advantage that the "abstracts" it contains differ from the conventional type in that they are often so complete that it is not necessary to refer to the original works. If in fact the editors had managed to condense articles without loss, there might be something to be said for this approach, but in the reviewer's opinion this has in many cases not been seriously attempted, despite long quotations and profuse use of tables, graphs, and charts. On comparing some of the abstracts with the original articles, it would seem that this "scissors and paste" technique has defeated the authors' intentions without reducing the work load on the reader. Consider a few instances—

"Variation of Fineness of Staple Fibres", by D. H. Morton (*J. Textile Inst.*, **47**, T 422 (1956)), abstracted on p. 159— In the view of one well qualified to judge, the abstractor has failed to grasp a major point made by the author. Whilst correctly stating that there is a linear relation between strength and denier and that with fibres in which the denier varies considerably, such as wool or Fibrolane, labour can be saved by making measurements of individual fibre denier, the abstractor does not point out that the results which are obtained in this way might in fact be quite different from the results obtained by making measurements of average fibre denier.

"Lightfastness Testing", by K. McLaren (J.S.D.C., **73**, 121 (1957)), abstracted on p. 651— This appears to be a valid abstract of Mr. McLaren's paper and does give briefly a clear idea of what the paper is about insofar as to have read the abstract would be better than not to have been aware of the paper. The interested reader would certainly be directed to the original.

"Flame and Glow Resistance of Chemically Modified Cotton Cellulose", by E. Pacsu and R. F. Schwenker (*Text. Research J.*, **27**, 173 (1957)) and "The Procion Dyes", by W. Sekules (*Textile World*, **107**, 65 (Aug. 1957)), abstracted on pp. 559 and 903 respectively— In both cases the abstract is so close a paraphrase of the original that there seems to have been little point in not just reproducing the articles. In the former instance, the abstract is about the same length as the original article and differs from it only in several minor respects. This criticism applies equally to the latter article, and this is in any case unnecessary, because on p. 705 we have "Reactive Dyes", by T. Vickerstaff, which gives the same information in greater detail.

The majority of the abstracts are taken from *Text. Research J.*, *J. Textile Inst.*, United States Patents, *Amer. Dyestuff Rep.*, and J.S.D.C. in that order. From the point of view of obtaining value for money, the volume under review costs $45, i.e. approx. £16, the *Textile Research Journal* can be obtained for $21, i.e. £7 10s., and the *Journal of the Textile Institute* subscription is £7 7s.

Few foreign journals are covered, and few papers are abstracted. The indexing leaves something to be desired, and, despite a claim in the preface that 1957 is covered, very little later than September 1957 is included.

Altogether not a very good buy.

S. Burgess

Ververij-Beginselen
en Onderwerpen die daarbij aansluiten

By J. Nunnikhoven. Enschede: "De Tex" 1958. Pp. 255. Price, 14.75 florins.

As the title indicates, this publication sets out to deal with the principles of dyeing and allied subjects. Such ambition, however, is set in perspective in the Foreword, which clarifies the aim to be on the one hand the presentation of theoretical principles as clearly as possible, and on the other hand to review the difficulties of application techniques. The further point made that the text is treated from the point of view of the dyer and textile chemist may be said to put the book in focus.

There are 37 chapters, ranging from the material to be dyed, through chapters dealing specifically with all the usual classes of dye, including the cellulose-reactive type, through fastness properties, pH-values, light and colour, water, bleaching, and even the organisation of a textile factory— a formidable programme indeed to be achieved or even attempted within the scope of a book of 255 pages.

A number of the chapters are divided into Parts A and B, the declared aim being to treat the subject-matter in a simple manner in Part A, leaving greater detail to Part B. Much of the material, especially that in Part A, is on the lines of the information copiously supplied by dye manufacturers except that trade names for the most part have been suppressed. One forgives the "commercial" for *Indanthren* on p. 52. Parts B contain some formulae and chemical equations not likely to be beyond the dyer and textile chemist for whom the book was written, or the student to whom it could be useful.

One unusual feature of this book is the complete absence of illustration. This in spite of a chapter on continuous dyeing (pp. 123–126), where description of such installations as the Standfast molten-metal machine must be understood from the written word.

In general the subject-matter is well set out in clear type, and reference is facilitated by the numbered-paragraph system adopted and the serviceable synopsis of contents (pp. 249–255). If on the one hand the book can be said to achieve its aim of presenting a very wide range of facts in a manner suitable for the type of reader for whom it was devised, it must be realised that condensation has been essential, and on individual subjects it may cause disappointment. A random example here would be the seven lines of print which cover the continuous dyeing of yarn.

E. Marney

Printed Textile Design
(How to do it series No. 74)

By Terence Conran. Pp. 95 with three plates in colour, 46 plates in half-tone, and 3 line drawings. London and New York: The Studio. 1957. Price, 25s. 0d.

This is not an easy book to review. It is always an easier task for a reviewer when a book falls into an established classification such as instructional, aesthetic, historical, practical or is, in itself, a review of current ideas and idioms in textile design. This particular book is impossible to classify. It attempts to deal with all the aspects noted above, with in addition a chapter giving useful and practical advice on selling designs to manufacturers.

The book is well produced with about 120 illustrations and diagrams, some in colour. The illustrations cover historic and contemporary textiles, dress designs, examples of interior decoration, ceramics, and other objects of industrial design. The illustrations are, on the whole, well chosen, and should stimulate and encourage

students of textiles to study examples of good design in many different media and periods. The text, however, may be criticised on several counts. It is surely unnecessary in a book on printed textile design to devote two chapters to elementary weaving and textile fibres: it must be assumed that students either possess that knowledge or can obtain it by reading some of the excellent text-books available. In the same way, the amount of space devoted to the technique of screen-printing is, in the writer's opinion, not really of great value to the student of design. The making of one screen combined with a practical demonstration of the process should be enough for anyone to understand the limitations of designing for it. It is felt also that not enough emphasis is placed upon sound training in draughtsmanship, study of colour— physical and aesthetic— and upon variety of styles in textile design. After all, the professional designer should be skilled in designing in many idioms and not be confined only to that of the moment, which might well be ephemeral. To quote one of the writers in the book, Tibor Reich—

> Designers of many modern fabrics seem to believe that all that is required is that their work should be bold and modern, and they thoughtlessly use the various clichés of blatant contrasting shapes, lines and colours, often derived from earlier work of more sensitive designers.

While many of the illustrations show good examples of modern textile design from good designers, an unfortunate tendency may be discerned in these as in other examples of the so called "contemporary" style. This is a kind of breadth of treatment— no doubt occasioned by the screen-printing process— which rapidly degenerates into a deliberate roughness and crudity. It is surely possible, and desirable, that modern and original ideas should be expressed in fine engraving and fine printing, thus preserving the traditions of British craftsmanship in printed textiles.

J. Chirnside

Knižnica L'udového Umenia

Sväzok 2

L'udová Modrotlač na Slovensku

By Jozef Vydra. Bratislava: TVAR Výtvarné Nakladatel'stvo. 1954. Pp. 207 including 165 plates. Price, Kčs. 52.

The volume under review is the second in a series of books dealing with folklore and regional crafts in Slovakia. It describes the historical development and present position of folk blue-printing in Slovakia, as opposed to printing on an industrial scale. Emphasis is laid on one aspect of blue-printing, namely the application of Indigo for the production of the well known reserve style. This method is eminently suitable for adoption by farming-community artisans and does not require expensive equipment. Despite heavy pressure from the highly developed textile industry of Czechoslovakia, folk blue-printing still survives in some parts of Slovakia. We learn from the book that there are about 21 small printing works operating the old Indigo reserve process in Slovakia, eight of which are privately owned, whereas the rest have either joined printing cooperatives or been nationalised. The reason for their survival is probably the great Slovak tradition of national costumes, varying from village to village. Only the local craftsman and artist are capable of expressing the people's artistic feelings.

The author describes by way of introduction the historical development of textile printing in Europe with special reference to the uses of Indigo. Reserve-printing with Indigo was introduced into Slovakia from Holland via Germany. The first blue-print on textile was produced in Slovakia in 1798, but, judging from the recipes given in the book as examples of present-day procedures, hardly any changes or improvements can have been introduced since the earliest days of Indigo reserve-printing. The author holds the view that Indigo reserve-printing expresses better than any other method of Indigo printing the true artistic feelings of the people. In his eyes, direct printing was more closely associated with the mass production of textiles, and caused a decline in taste. Good taste is equated in the book with popular taste, a rather superficial assumption.

Printing methods are completely empirical. Although so many considerably faster dyes than Indigo have been introduced, and processes developed which permit the production of the same and even more varied colorations with improved fastness properties, many of the peasant communities still accept Indigo prints as representing the highest standards of fastness. Its poor rubbing fastness is acclaimed as a sure sign of its excellence. One cannot help feeling that this type of textile processing is now doomed. The book gives a list of families and people still engaged in Indigo printing and dyeing, but this will be of interest only to the local historian, the student of folklore, and the collector of national costumes. The history of European printing and dyeing has been adequately covered by many textbooks, Indigo having enjoyed an especially exalted position. The present book can, therefore, add very little to our general knowledge of this particular field. Identical printing methods and colorations and very similar designs will be found all over Central and South-eastern Europe where Indigo reserve printing is carried out by peasant artisans. However, the paragraph on the production of the wooden or metal printing blocks is excellent and exhaustive, although the author is on less safe ground when he attempts to introduce a few chemical facts into processes which must be regarded as obsolete. The author is also at odds when he has to make brief reference to more modern dyes, which is perhaps not surprising in a book which is addressed primarily to the specialised historians of regional arts and crafts.

The book is not only illustrated by many pictures in the text, but has also a supplement of 117 excellent coloured plates showing prints and national costumes.

P. Krug

Problems in Wood Chemistry

Jerusalem: Weizmann Science Press of Israel. 1957. Pp. x + 137. Price, $6.00.

This book contains lectures and discussions which took place during the meeting of the United Nations Food and Agricultural Organisation Technical Panel on Wood Chemistry in Israel in 1956. There are seven lectures, each reviewing recent developments in some aspect of wood chemistry or technology and provided with an extensive bibliography. The title of the first lecture, *Radiation Chemistry and Wood*, by Professor H. Mark (Brooklyn), is really a misnomer, since the paper consists of a very clear account of the effects of nuclear radiations on high polymers generally which may be read with profit by all interested in polymer science.

The remainder of the lectures fall into two groups, the first of which is concerned with the chemistry, morphology, and properties of certain constituents of wood. Professor Giertz (Trondheim) contributes a short account of the compound middle lamella of wood— the intercellular substance plus adjacent primary walls of contiguous cells. This is shown to be largely lignified, cellulose occurring in the primary walls. Dr. Lewin, of the Fibres and Forest Products Research Institute of Jerusalem, gives an exhaustive review of the middle lamella of bast fibres and its influence on their properties, with particular reference to jute and flax. Differences in chemical reactivity between constituents of the middle lamella and the cell wall are shown to account for most of the differences in behaviour to chemical treatments between bast fibres and cotton. Professor K. Freudenberg (Heidelberg) briefly discusses the problem of carbohydrate bonding in wood.

The other group of lectures is concerned with the uses of synthetic resins in the utilisation of wood and wood products, particularly in lamination. Professor Mark, in a lecture on *A Few Principles of Adhesion*, provides a very clear picture of fundamental principles from both the molecular and the thermodynamic approaches. Professor E. C. Jahn (Syracuse, N.Y.) reviews the uses of resins with wood and the type of products obtained. Dr. Ott and Dr. Heiberger (Food Machinery & Chemical Corpn., N.Y.) discuss many new developments in synthetic resins for wood adhesives. There is also an extensive review of recent literature on synthetic adhesives for wood. The book concludes with an account of the institutions and industries visited by the members of the Panel in Israel. Readers of this *Journal* will be interested in the account of the work of the Institute for Fibres and Forest Products Research in Jerusalem. Basic and applied research on existing and potential raw materials in Israel includes work on a new process for rendering wool shrink-resistant and non-felting and a fundamental study of crimp in fibres. Members of the Institute staff have been primarily responsible for the production of this book, which, although concerned mainly with wood, contains much of interest to the polymer chemist and the fibre technologist.

W. R. Moore

Le Mécanisme de la Vision des Couleurs
Physiologie—Pathologie

By J. Ségal. Pp. 351 + 1 colour plate. Paris: G. Doin & Cie. 1953. Price, 3200 francs.

Mechanismus des Farbensehens
Physiologie—Pathologie

By J. Ségal. (translated from the French by H. Gehne). Pp. xv + 283 + 1 colour plate. Jena: VEB Gustav Fischer Verlag. 1957. Price, DM 32.00.

This book is a monograph in which the author puts forward a novel theory of the mechanism of colour vision. The basic idea of the theory is that the elements of different sensitivity lie not in a mosaic as normally assumed but in separate layers of the retina, the colour sensitivity of the lower layers being modified by absorption in the outer layers. The theory thus ascribes to the retina a *modus operandi* very similar to that of a tripack colour film, even the order of the sensitive layers being the same. In support of his theory the author adduces the following main considerations—

(1) The failure to identify three different types of cone.

(2) Apart from certain iron and copper compounds, all known substances have the requisite absorption characteristics, to account for the spectral sensitivity, at the red end of the spectrum only in the crystalline state. A suitable crystalline material has been found in the pigment layer of the retina but nowhere else.

(3) An appropriate sensitivity for a red receptor requires in addition that blue and green radiation should be subject to prior attenuation.

(4) The author claims to have identified the necessary neural connections to the different layers.

This is not the place to consider in detail the physiological arguments used to support the theory. Suffice to say that the physiological implications are thoroughly considered. The applications to such subjects as adaptation and defective colour vision are also dealt with. As opposed to some modern theories, this theory is strictly trichromatic, and may be regarded as an attempt to provide a physiological basis for the Young–Helmholtz theory. The book will thus appeal mainly to those interested in the physiology of colour vision rather than to those interested in the practical application of colour theory.

F. L. Warburton

Identification of Textile Materials

The Textile Institute. 4th edition 1958. Pp. 148. Manchester: The Textile Institute. Price, 27s. 6d.

"The Committee has always had the avowed aim of assisting practising Textile Technologists and those aspiring to be such." With the appearance of each new edition of this book it must have been gratifying to the would-be user of it to be reassured on this point, for each has been considerably larger than its predecessor, thus bearing mute testimony to the ever more rapid growth of the textile fibre field. Thus the latest edition is more than one-third larger than its predecessor, the section on fibre properties has been largely

rewritten, and there are nearly twice the number of photomicrographs, including some in colour.

The general layout remains the same, viz. an encyclopaedic section on fibre properties followed by the schemes of analysis, with notes on methods of test, and the photomicrographs. The developments of the last few years have led the Committee to adopt a radically new method of presentation and arrangement of the scheme of analysis itself, since the introduction of so many new fibres has made it practically impossible to produce a complete scheme in a single-sheet format. An introductory table has been provided to enable anyone using the scheme to appreciate the general approach. This consists in a preliminary examination of the material to determine whether it is homogeneous, followed, if it is so, by a sorting test by heating, to separate the older natural and man-made fibres from the cellulose acetates and the newer synthetic fibres. To sort out the latter, use is made of the presence or absence of nitrogen and chlorine to separate them into manageable groups, and the individual members of each group are then positively identified by determining their solubility in selected reagents.

No complete scheme of analysis which does not include microscopic examination is given, but a simplified scheme based solely on solubility tests carried out in test-tubes is included which might be useful if no microscope is available.

The scheme of analysis suggested for dealing with blends of fibres is new. The reference to it in the introduction—"Single sorts of fibres are easier to identify than are the constituents of blends of fibres. Nowadays fibre blends are being widely used commercially"— may sound to some like an understatement! The experienced worker will no doubt have his own approach to this problem, but it is very desirable that a systematic scheme be provided. The principle followed here is to treat the fibre mixture successively with various reagents, each of which will dissolve a group of fibres. If one or more fibres of a particular group are found to be present, the original specimen or the residue after evaporation of the solvent is treated successively with a further series of reagents in a prescribed order until one is found in which the fibre dissolves, and the latter is identified thereby.

This edition, like its predecessor, is bound in cloth. Whether or not this is the best form of presentation is difficult to say. It might conceivably be advantageous to be able to separate the tables proper from the rest of the text and the photomicrographs, since it is this section that will be most used, at any rate by the student of textile technology and the beginner in the works laboratory. The size of the volume has increased by one-third, but the price has considerably more than doubled. However, in view of the comprehensiveness of the treatment of the subject this can be borne. The Committee claims that the redesigned scheme of analysis should make it a more powerful analytical tool for dealing with new fibres, new finishes, and mixtures of fibres. Their efforts deserve to be welcomed.

C. B. STEVENS

A History of Industrial Chemistry

By F. Sherwood Taylor. Pp. xvi + 467. London: W. Heinemann Ltd. 1957. Price, 30s. 0d.

With the present-day tendency for even tinctorial technologists to run a grave risk of knowing little or nothing of any technology save their own, books like the one under review need no excuse. The great danger would seem to be that, with so large a canvas to cover, the author could so easily produce an unbalanced account arising from undue prominence being given to his own particular interests. The author's declared intention in this instance was the presentation of a short history of industrial chemistry from the earliest times to the present day, and with his wide experience of popularising the history of science, it is not surprising that in this, his last book, Dr. Taylor produced a most readable as well as a most informative book.

It is interesting that he has included not only accounts of the development of the chemical industry from prescientific times to the atomic era but also an outline of the development of scientific thinking which has been an essential and causal part of industrial chemistry since the early eighteenth century, the history of which cannot be understood without reference to it.

Naturally, readers of the *Journal* will be particularly interested to discover the amount of space allotted to the colouring of textiles and the production of colouring matters for this purpose. It is to be hoped that they are not too chastened when they find that the main reference to dyeing is in a generous chapter in the section devoted to prescientific chemical industry! We are told, and may sometimes believe, that dyeing "was perhaps the most static of the arts and was always (and ever will be) something of a mystery." The origin and application of the dozen or so dyes available up to 1856 are dealt with in most interesting fashion, and our indebtedness to Perkin and his successors should be increased when Dr. Taylor roundly declares that even the cardinals of medieval times were arrayed in a more sober range of crimsons, clarets, and indigos rather than the scarlets and ultramarines of the later painters' fancy. The manufacture of synthetic dyes is discussed in a comparatively few pages, since it must compete for space with the man-made fibres, plastics, petroleum products, and the even more recent wonders of our day. However, the main steps in the development are covered.

The book is well documented for further reading, is well produced, and is illustrated with many black-and-white diagrams and drawings and photographs. It is an authoritative and fascinating account of, to quote the author once more, "advance on one particular front towards the solution of man's impotence and want."

C. B. STEVENS

New Books received

Chemical Society Symposia, Bristol 1958. Developments in Aromatic Chemistry. Applications of Electron and Nuclear Resonance in Chemistry. Recent Work on the Inorganic Chemistry of Sulphur. Special Publication No. 12. London: Chemical Society. Pp. vii + 401. 42s. 0d.

Tables of Interatomic Distances and Configuration in Molecules and Ions. Special Publication No. 11. London: Chemical Society. 1958. Pp. 384. 42s. 0d. ($6.00).

The Encyclopedia of Chemistry. Supplement. George L. Clark, G. G. Hawley, and W. A. Hamor (editors). New York: Reinhold Publishing Corpn. (London: Chapman & Hall Ltd.). 1958. Pp. vii + 330. 80s. 0d.

Färberei-Praxis. Willi Festerling. Heidenheim (Brenz). Germany: Verlag Alfred Halscheidt. *Teil I—Das Färben nativer Fasern. Baumwolle, Flachs, Hanf, Jute, Kokos, Stroh.* Pp. 104. DM 12.80. *Teil II—Praxis der Baumwollfärberei.* 1957. Pp. 154. DM 16.80.

Flammable Liquids are Dangerous. London: Fire Protection Association. March 1958. Pp. ii + 4. Gratis.

Wollschädlinge und ihre moderne Bekämpfung. A. Herfs and H. Stötter. Leverkusen: Farbenfabriken Bayer AG. [1958.] Pp. 78. Gratis.

Paint Film Defects. Their Causes and Cure. Manfred Hess. London: Chapman & Hall Ltd. 1958. Pp. xvi + 544 + 87 illustrations. 75s. 0d.

Physical Chemistry of High Polymers. Maurice L. Huggins. New York: John Wiley & Sons Inc. (London: Chapman & Hall Ltd.). 1958. Pp. xiii + 175. 52s. 0d.

Dizionario tessile laniero. Inglese–Italiano, Italiano–Inglese. Schio (Vicenza), Italy: Lanerossi. [1958.] Pp. 160. Lire 300.

Methoden der Organischen Chemie (Houben–Weyl). Band **XI**. *Teil 2. Spezielle chemische Methoden. Stickstoffverbindungen II und III.* Edited by E. Müller. Stuttgart: Georg Thieme Verlag. 4th edition 1958. Pp. xlviii + 840. DM 155.00.

Fulling Mills. A Study in the Application of Water Power to the Woollen Industry. R. A. Pelham. London: Society for the Protection of Ancient Buildings. 1958. Pp. 16 + iv plates. 3s. 0d.

Mercerisation. Hans Rau. Heidenheim (Brenz), Germany: Verlag Alfred Halscheidt. Pp. 57. DM 8.60.

Chemie der Azofarbstoffe. Heinrich Zollinger. Basel: Birkhäuser Verlag. 1958. Pp. 308. Swiss francs 36.25 (DM 36.25).

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

Badische Anilin- & Soda-Fabrik AG.

Basolan Fast Blue FRL— This acid dye gives bright blues on wool and polyamide fibres and is recommended for use alone and in mixtures on yarn and cloth. Fastness figures on wool include— Light 5, washing (*b*) 3–4, perspiration 2–3.

Helizarin Brilliant Red BB— This pigment is suitable for direct printing and pad-dyeing to give very bright bluish reds when resin-bonded to textile materials, a particular feature being the very high colour yield obtained. Fastness figures include— Light 7, severe washing 5, chlorine 5.

Helizarin Brown R— This pigment gives reddish browns of very good fastness when resin-bonded to textile materials. It is mainly recommended for textile printing, being very economical in use and giving prints of outstanding fastness to light. Fastness figures include— Light 8, washing at the boil 5, chlorine (*b*) 5.

Ciba Ltd.

Cibacron Black BG— This reactive dye gives greys to blacks on all types of cellulosic fibres when applied by either padding or batchwise exhaustion methods. The dyeings obtained have very good wet fastness, show virtually no change in hue in artificial light, and are stable to resin finishes, rubberising, and coating with polyvinyl chloride. In addition to a comprehensive selection of dyeings on viscose rayon and cotton yarn and cloth, eight dyeings on either viscose rayon or cotton yarn, dyed by the exhaustion method, six on cotton gaberdine, dyed by the pad–thermofixation method, and a further six on cotton and viscose rayon knitted cloth, dyed by the exhaustion method, show the usefulness of this dye as a component of mixture dyeings.

Fastness figures of a black dyeing on cotton include— Light 6–7, washing (E.C.E. *b*) 4, perspiration 4.

Dow Chemical Co.

Dow Light Absorbers— This booklet describes the structure, properties, and applications of four products for incorporation in plastics and other compositions to inhibit degradation by ultraviolet radiation. These are *salol* (phenyl salicylate), *light absorber TBS* (4-*tert.*-butyl phenyl salicylate), *light absorber HCB* (5-chloro-2-hydroxybenzophenone), and *light absorber DBR* (2:4-dibenzoylresorcinol). A few general observations on the process of photodegradation in plastics are included together with photographs illustrating the effectiveness of these products when incorporated in various substrates.

Imperial Chemical Industries Ltd.

Caledon Direct Black BN— This vat dye gives blacks of excellent fastness when applied direct to cellulosic fibres. It is recommended for application by Method 4 at 60°c., but it will withstand dyeing at temperatures up to 90°c., and is sensitive to the restraining and levelling action of Dispersol VL. The FD brand is recommended for all leuco vat dyeing and pigmentation methods, including the prepigmentation of viscose rayon cakes. Fastness figures on cotton include— Light (Bombay) 7–8, washing (Test No. 5, 5 times at 97–100°c.) 4–5 (redder), soda boiling 4–5, hypochlorite 5.

Caledon Olive RMW— This vat dye gives olives markedly redder in hue than are obtained with the MW brand. It is preferably applied by Method 2 at 50°c., but is suitable also for application at temperatures up to 90°c., and the use of higher temperatures and Dispersol VL are effective methods for obtaining level dyeings. Like the MW and OMW brands, it is very suitable for application in the Standfast molten-metal machine and by prepigmentation methods. It provides a convenient basis for producing military colours with satisfactory infrared reflectance characteristics. It is also of interest for fast dyeings on silk. Fastness figures on cotton include— Light 7 (Wilmslow), 6–7 (redder) (Bombay), hypochlorite 4–5, soda boiling 3–4.

Caledon Yellow 4GL— This vat dye gives greenish yellows of excellent wet fastness and very good light fastness on cellulosic fibres and silk. In combination with Caledon Jade Greens XBN, XN, and 2G and Green 7G, with which it is compatible in dyeing behaviour, yellowish greens of high light fastness may be obtained. It is slow-dyeing and has good migrating power on cotton. It is not recommended for high-temperature leuco dyeing. Peroxy compounds should be employed for reoxidising the leuco compound on the fibre. Dyeings are not unduly prone to photochemical degradation. Fastness figures on cotton include— Light 6–7 (Wilmslow), 6–7 (Bombay), hypochlorite 5, soda boiling 5.

Procion Dyestuffs in Textile Dyeing: Natural Silk and Nylon: Volume 2— This card describes a further nine reactive dyes of the Procion range, which (with one exception, Brilliant Yellow H5G, which is not recommended for dyeing silk) are of interest for dyeing silk and nylon. Dyeings on nylon staple yarn and spun silk yarn are included.

Dyestuffs for Terylene Polyester Fibre. Disperse and Azoic Dyes. Volumes 1 and 2— These two cards of the now standard loose-leaf type contain

details of 24 disperse dyes and 11 azoic combinations. Dyeings in three depths on continuous-filament and spun yarn are included in the case of the disperse dyes. With the azoic combinations, dyeings in one depth only are shown. Volume 2 also contains 12 dyeings on continuous-filament yarn produced with mixtures of disperse dyes.

PROCION BLACK HG— This reactive dye gives neutral greys to blacks, particularly on mercerised cotton and viscose rayon, and is also of interest for navies in combination with Procion Blue HB and Procion Rubine H2B. It may be applied by all the established procedures for the Procion H brands, including a hot batch-dyeing technique, but in this case blacks are obtainable only on viscose rayon, and 80–100 parts of salt per 1000 parts of dye liquor must be added. Fastness figures for a black on viscose rayon include— Light 6–7, washing (Test No. 5, 5 times at 100°c.) 4–5.

PROCION RUBINE B— This reactive dye is of the more reactive type and is suitable for application by both steaming and non-steaming methods to give full bluish reds by direct printing on cellulosic fibres. It is not recommended for use alongside Soledons developed by nitrite, but is unaffected by aftercoppering. White resists are obtainable by using Resist Agent PR. Fastness figures on cotton include— Light 6–7, washing (Test No. 5, 5 times at 100°c.) 4–5.

PROCION SCARLET G— This reactive dye gives very bright yellowish scarlets on cellulosic fibres and is of interest for both pad and batchwise application, optimum fixation by the latter method being obtained by using tribasic sodium phosphate when dyeing cotton and soda ash with viscose rayon. It is compatible with other cold-dyeing Procions and is useful as the red component of fawns, browns, and greys. In printing it is primarily of interest in self-colours. Aftercoppering causes dulling and bluing, and treatment in acidified nitrite as used for developing Soledons results in slight yellowing. Fastness figures for a dyeing on cotton include— Light 4, washing (Test No. 5, 5 times at 100°c.) 4.

PROCION DYESTUFFS AS RESISTS UNDER ANILINE BLACK— By using Procion dyes, coloured resists may be obtained superior in brightness and novelty of colour to those obtained using Brentogens, Soledons, or vat dyes. An effective resist for Aniline Black which is also capable of fixing the reactive dye is obtained by increasing the alkalinity of the print paste by adding sodium carbonate and magnesium oxide. Since the Procion dyes appear to react preferentially with aniline or its salts rather than with cellulose, it is necessary to ensure that the reaction with the latter has occurred to a considerable extent before the components for forming the oxidation black are applied. Details are given, and four examples of roller-printed resist styles are included.

HEXAGON DIGEST. No. 26 (March 1958)— Articles in this issue include— *The Effect of pH in the Batchwise Dyeing of Procion Dyestuffs*, by A. M. Wooler, *The Relationship between the Rheological Properties of Letterpress Printing Inks and their Behaviour in the Duct of a Printing Machine* by N. Casson, and *The Cambridge Textile Extensometer: Modifications and Applications* by Miss S. D. Fletcher.

TECHNICAL INFORMATION LEAFLETS— *Dyehouse No. 412. Pad–Roll Dyeing of Nylon, Secondary Cellulose Acetate, and Triacetate Fabrics*—Details are given for applying disperse dyes to cellulose triacetate, and the Nylomine dyes, to secondary cellulose acetate rayon and nylon. The Nylomine dyes are preferred on the latter because, being soluble in water, there is no risk of "specking", and cleaning down between runs is easy. In addition, they are much superior in fastness to light and wet treatments on nylon and to wet treatments on secondary cellulose acetate rayon to, and in most cases give a higher colour yield than, the disperse dyes.

Dyehouse No. 414 (replaces No. 207). *Levelling of Water-soluble Dyes on Nylon*— This note describes steps that can be taken to improve the levelling properties of acid, chrome, Solacet, Ultralan, and Nylomine dyes on nylon. In particular, the value of Carbolan Salt A for this purpose has been investigated and the results are tabulated.

Dyehouse No. 415. The Dyeing of 'Terylene' Polyester Fibre: Supplement No. 8— An alternative method is described for producing an azoic black with Dispersol Diazo Black B and Brenthol OT for use particularly where there is risk of some settling out of the Brenthol from suspension or excessive filtration of it on to the outside of the package.

Dyehouse No. 416 (replaces No. 217). *Mélange (Vigoureux) Printing of "Terylene" Polyester Fibre*— A process is described which utilises the equipment conventionally employed in the mélange printing of wool sliver.

Dyehouse No. 418.— Alcian Dyestuffs: Dyeing of Wool–Cellulose Unions— Alcian X dyes, particularly Alcian Blue 8GX 300, are of interest for dyeing the cellulosic portion of wool–cellulosic fibre mixtures from a dyebath containing 5–10 parts of acetic acid (30%) per 1000 parts. Subsequent treatment in soda ash solution at 60°c. develops maximum fastness properties. Virgin wool is virtually undyed, but heavily damaged wool may be dyed more deeply than the cellulose. Where it is desired to "fill-in" the wool, Durazol Blue 6GW (or Durazol Printing Blue 6G) is recommended for this purpose.

Dyehouse No. 419 (replaces No. 373). *Light Fastness of Dyestuffs*— The higher fastness rating expected when dyeings on fibres sensitive to differences in humidity are exposed in a sunny country is chiefly observed with cellulosic fibres, azoic dyeings being particularly affected in this way. Conversely, patterns sensitive to differences in temperature would be expected to give a lower rating in the sunnier country, and such is found chiefly to be the case with the hydrophobic fibres.

Dyehouse No. 420. Dispersol AC: An Alternative Dispersing Agent for Dyeing "Terylene" and Cellulose Triacetate Fibre— In the dyeing of 100% cellulose triacetate or "Terylene" to heavy depths with Duranol Blue G, Dark Blue TG, and Navy Blue BN, Dispersol AC is preferred to Lissapol C or D as dispersing agent. It is not recommended as a general replacement.

Dyehouse No. 449. "Terylene" Polyester Fibre. The Production of Pale and Medium Shades of High Fastness to Light— Where pale colours of maximum fastness to light are required and when fastness to heat-treatments is of secondary importance, e.g. for furnishings, dyeings based on Duranol Red 2B, Duranol Blue TR, and Dispersol Fast Yellow GR have been shown to be superior to all others. Dyeings having a light fastness of 6–7 or better and fading on tone are obtained by dyeing at 130°c. Dyeings produced using Tumescal OP have a light fastness only 0·5 grade lower.

Dyehouse No. 451. Procion Dyestuffs: The Pad (Alkali)–Batch (Cold) Method of Dyeing Cellulosic Piece Goods. Supplement No. 1— Details are given of the use of (1) a 3 : 1 mixture of soda ash and sodium bicarbonate as the alkali when applying the cold-dyeing Procions by the pad–batch (cold) method and (2) 5 parts of caustic soda per 1000 parts of padding liquor when applying the H brands by the same method.

Dyehouse No. 452. Application of Procion Dyestuffs to Natural Silk. Supplement No. 1. Fastness to Scrooping— Scrooping of silk dyed with Procion dyes using tartaric acid results in some loss in wet fastness on storage owing to acid hydrolysis of the dye–fibre linkage. A neutral "scroop" free from this defect may be obtained by padding the material with dispersion of 3–4 parts of Cirrasol SF per 1000 parts of water at room temperature and drying without rinsing.

Dyehouse No. 453. Viscose Rayon: Processing Aids— An outline is given of the uses of ten auxiliary products in the manufacture and processing of filament and staple viscose rayon.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

Developments in the Pressure Dyeing of Yarns
Jagri G.m.b.H.
Text. Manuf., **84**, 426–427 (Aug. 1958)

Pressure is raised in the dye vessel by means of a small pressure cylinder with piston to which weights can be added to adjust its magnitude; this requires no second pump or additional energy. The direction of liquor circulation (inside ⇌ outside) can be reversed manually or automatically, and samples can be withdrawn directly from the dyed batch without interrupting the dyeing process. All controls are situated on a separate panel and fully automatic operation may be arranged. A new carrier enables hanks to be dyed in round machines. There are two photographs of the plant and one of a laboratory model. J.W.D.

Simple Device to facilitate Penetration of Compact Samples
G. Menschel
Textil-Praxis, **13**, 839 (Aug. 1958)

The material to be dyed is placed between two perforated stainless steel discs, mounted on a vertical spindle. A crank shaft driven by a small electric motor provides an up-and-down agitation in the dye liquor. L.A.T.

PATENTS

Scouring or Dyeing
Southalls (Birmingham) and Jackson & Brother
BP 802,685

Cloth is continuously fed around a hollow rotating drum immersed in the treating liquid, the interior of the drum being heated so that it causes the liquid to boil. C.O.C.

Conveying Festooned Fabric
Flaxall Products *BP* 802,576

An endless conveyor includes an upper horizontal run and a series of parallel, interspaced, interconnected, thin flat bars. Each bar engages and folds over itself the fabric entering the apparatus and carries the fabric from one end of the upper run to the other so that the fabric is carried festooned through the apparatus. Means are provided to engage the bars and stand them on edge in the upper run and urge them into close proximity. C.O.C.

Drying Fabric, Paper, etc.
J. Dungler *BP* 802,296

Modification of *BP* 773,606 (J.S.D.C., **73**, 428 (1957)). The radiant elements both irradiate the fabric and heat the air circulated through the drier. C.O.C.

Open-side Multiple-roll Calender
McKiernan-Terry Corpn. *USP* 2,815,531

A calender of open side construction enabling ready removal, replacement and changing of the rolls. It has variable drive and pressure means enabling it to be used for such different operations as rolling, friction, schreinering and embossing. C.O.C.

Continuous Rapid Pleating of Fabric
Cranston Print Works Co. *USP* 2,821,237

Apparatus which enables continuous warpways pleating of fabric at up to 50 yd./min. C.O.C.

Screen Printing Machine
Whitebirk Weaving Co. *BP* 802,728

The squeegee mounting carries two squeegees and the mechanism which drives it is on supports which can be reciprocated along the length of the machine at different heights during the forward and backward strokes of the mounting thus enabling the appropriate squeegee to be brought into register with the screen at the start of each stroke.

BP 802,729

A horizontal screen and squeegee are vertically adjustable to a height at which a block of cloths to be printed can be placed between the screen and the table. As each cloth in the block is removed after being printed, the screen and squeegee adjust themselves automatically to the height needed to print the next cloth. C.O.C.

Driving Mechanism for the Shafts of Rollers in Roller Felting Machines
William Bywater *BP* 802,627

Drive for making the rollers reciprocate along their axes in addition to rotating. C.O.C.

Handling Tubular Knitted Fabric
Wolsey *BP* 802,750

Wale spirality is automatically removed before drying by passing the fabric over a stretching device and urging at least some of the stretched fabric against a rotary roughened guide so as to cause the fabric to rotate. C.O.C.

Tubular Knitted Fabric Dryer
M. G. Fernandez *USP* 2,821,769

The fabric is drawn up a cylinder while hot air under pressure is discharged into the interior of the tube of fabric both to dry it and to keep it at a constant distance from the wall of the cylinder. C.O.C.

II—WATER AND EFFLUENTS

PATENT

Treatment of Boiler Feed Water
ICI *BP* 802,875

Formation of scale and incrustation is avoided by adding a soluble magnesium compound together with a soluble polyphosphate or polyphosphate and tannin to the feed water before it enters the pre-boiler equipment or cooling systems. C.O.C.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Complexones. XXIX—A Special Kind of Large Chelate Effect
G. Schwarzenbach, H. Senn, and G. Anderegg
Helv. Chim. Acta, **40**, 1886–1900 (Oct. 1957)

Complexing agents of the type $(HOOC{-}CH_2)_2 = N{-}(CH_2)_n{-}N = (CH_2{-}COOH)_2$ are investigated with *n*-values from 2–8. The stability constants of the 1 : 1 -complexes of Ca^{2+}, Cd^{2+}, and Hg^{2+} are determined for nearly the whole series, and also a few values of Mg^{2+}, Sr^{2+}, Ba^{2+}, and Co^{2+}. In general, there is a strong decrease in complex stability when *n* is increased from 2 to 4, after which an almost constant value is reached. The mercury complexes behave exceptionally. Replacement of one or two CH_2-groups in the chain connecting the two nitrogens by –O–, –S–, and $-N(CH_3)-$, increases the complex stability to a great extent if new 5-membered chelate rings can be formed by coordination of this heteroatom. H.H.H.

Quaternary Ammonium Compounds of Polypeptide Character
J. Bolle, P. Ragon, T. Jullig, and D. Boido
Proc. 2nd Internat. Congress Surface Activity, **4**, 70–75 (1957)

These products are obtained by the action of fatty acid chlorides on the free amino groups of degraded proteins. The alkaline hydrolysis of gelatin, and the reaction of the resulting protein with chloracetyl chloride are discussed. The reaction of lauryldimethylamine, lauryldiethanolamine and benzyldimethylamine with the product is completed in 3–4 hr.; with lauryldiethylamine in 6 hr. The surface-active compounds resulting from the use of lauryl-(I), myristyl-, cetyl-, benzyldimethylamine (II); lauryldiethylamine, lauryldiethanolamine; equimolecular proportions of (I) and (II) were examined for wetting, foaming and bactericidal power. The benzyl radical made no contribution to the latter property. S.R.C.

PATENTS

Non-ionic Surface-active Agents
American Cyanamid Co. *USP* 2,816,882

The copolymers of acrylamide or methacrylamide and an acrylic or methacrylic ester of a saturated aliphatic alcohol of 8–22 C are non-ionic surface-active agents. C.O.C.

Surface-active Agents
FBy *BP* 802,642

Compounds of formula $R \cdot NH \cdot CH_2 \cdot A(OC_nH_{2n})_x \cdot Y$ (R = monovalent aliphatic or *cyclo*aliphatic hydrocarbon, A = Ar which may be substituted by Alk; Y = OH or sulphonic or carboxylic ester; *n* and *x* = > 2) are excellent agents for use in the wet processing, including dyeing, of textiles, particularly of wool. Thus *N-cyclo*hexylaminomethylnonylphenol octadecaglycol ether is used for washing wool in presence of acid. C.O.C.

Solid Emulsifying Agents
Patent & Licensing Corpn. *USP* 2,819,228

A negatively charged solid emulsifying agent, e.g., ball clay, kaolin and bentonite, is mixed with a little of a cationic surface-active agent, e.g. Armeen H.T.D. (a mixture of 25% hexadecylamine, 70% octadecyl and 5% octadecenylamine). The mixture is used for preparing aqueous emulsions of resins, rubber, and wax. C.O.C.

Detergent
Thomas Hedley & Co. *BP* 802,302

A detergent having low foaming properties but good heavy-duty cleansing efficiency comprises an anionic sulphate or sulphonate, at least the same weight of alkali metal polyphosphate, and, as a suds depressant agent, a mixture of at least three compounds—substituted fatty acids of 16–31 C and/or their alkali metal soaps. Of the depressant mixture 50% of the components are of > 15 C and ≮ 5% are of > 19 C. Thus to a mixture of Na alkyl benzene sulphonate (Alk of 12 C) (18 pts. by wt.), Na tripolyphosphate (48), silicate solids (6), miscellaneous (mainly water and Na_2SO_4) (28) was added 3% (on the total weight) of Hyfac 431 (a mixture of fatty acids derived from hydrogenated fish oil and containing approximately 8% myristic acid, 29% palmitic acid, 18% stearic acid, 26% arachidic acid, 17% behenic acid, and 2% oleic acid). C.O.C.

Spinning Lubricant for Wool
Nopco Chemical Co. *USP* 2,824,832

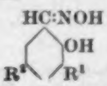
A blend of (1) an ethylene oxide-alkylated phenol condensate, (2) a blown oil, (3) mineral oil, and (4) a fatty acid or a mixture of a fatty acid and a fatty acid ester, is a good lubricant for wool during carding and spinning and is readily removed during scouring. C.O.C.

Copolymer containing Vinyl and Carboxy Groups for Warp Sizing
American Cyanamid Co. *USP* 2,819,189

Copolymers having recurring nitrile and COOX groups (X = H, Na, K, or NH_4) in a formula ratio of 1 : 0·30–1 : 0·75 attached to a long linear C chain and which in 5% aqueous solution have pH 5–9 and viscosity 5–200 cp. at 140°F. are excellent sizes for all types of fibres, both natural and man-made. They are readily removed by simple scouring, are non-flaking, resistant to abrasion and do not become gummy upon exposure to high R.H. for a long time. C.O.C.

Salicylaldoxime as Rotproofing Agent for Cellulose
Heyden Newport Chemical Corpn. *USP* 2,822,297

Compounds of formula—



(R^1 = Cl, Br or NO_2; R^2 = Cl or Br) are excellent rotproofing agents for cellulose. Thus 3-bromo-5-chlorosalicylaldoxime compares favourably in efficiency with Cu 8-hydroxyquinolinate but does not impart undesirable colour to the cellulose. C.O.C.

Aqueous Emulsions of Polymers for Use as Coatings, etc.
FBy *BP* 802,516

Aqueous emulsions of copolymers derived from ethylenically unsaturated monomers and containing at least one group $\cdot CO \cdot NR^1 \cdot CH_2 \cdot OR^2$ (R^1 = H or Alk; R^2 = Alk) are used to form sheets and coatings or for impregnating, and are then treated with an acidic substance and/or baked at 100–200°C. The properties of the products vary widely according to the components chosen, e.g. particularly flexible and strong films are obtained by using large amounts of butadiene while very flexible and soft coatings are obtained on fabrics by using the acrylic acid esters or vinyl ethers of higher alcohols. C.O.C.

Laundry Starch
American Tansul Co. *BP* 803,123

Addition of 3½% by weight of *hectorite* (a natural hydrophilic hydrated magnesium silicate), especially that occurring at Daggett, California, to starch applied to garments, etc. gives a finish which does not stick to irons or calenders, does not cause the layers of fabric to stick together and has a smooth, flexible handle. C.O.C.

Bacteriostatic Compositions for use with Starch
Scientific Oil Compounding Co. *BP* 803,080

An aqueous emulsion of a solution of a water-soluble phenol in a water-insoluble organic substance is used to prevent bacterial attack on starch sizes, etc., e.g. *o*-benzyl-*p*-chlorophenol (20 pts. by weight) is dissolved in di*iso*butyl ketone (5) and diluted with mineral oil (5). This is then emulsified in water (62) using K lignin sulphonate (5) as the emulsifying agent and gum ghatti (3) as stabiliser. Such emulsions can be diluted down to 1 part phenol per million without breaking down. C.O.C.

Water-repellent Agents and Plasticisers for Cellulose
FBy *BP* 802,541

The products obtained by treating molten salts of organic acids and primary aliphatic monoamines of > 13 C with epichlorohydrin consists of a mixture of compounds in which di-(γ-chloro-β-hydroxypropyl)-alkylamine salts of the organic acids predominate. They have varied uses. Thus, as they have high substantivity for cellulose they can be used as plasticisers for cellulose materials. Textiles, paper, leather, etc. impregnated with these products, and then baked, are given a water-repellent finish. C.O.C.

Chromium Coordination Complexes—Water Repellent Agents
Minnesota Mining & Manufacturing Co. *BP* 802,962

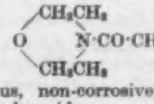
Perchloro fluoromonocarboxylic acids of 4–20 C are treated with chromium compounds containing at least one hydroxyl group, e.g. $Cl(CF_2 \cdot CFCl)_nCF_2COOH$ (*n* = 1–9) is treated with chromyl chloride in dichloromethane in presence of ethanol. The products are excellent water repellent agents for application to cloth, leather, etc. C.O.C.

Flame-resistant Finish by Use of an Alkali Metal Fluoride and Boric Acid or Anhydride
DuP *USP* 2,823,145

Sodium fluoride and boric anhydride or acid are fused together to form the compound $4NaF \cdot 5B_2O_3$ or its hydrate respectively. Both are readily miscible in cold water and are extremely effective agents for producing flame-resistant finishes on textiles, deposition of about 10% being generally preferred. C.O.C.

Solvent for Linear Polyamides
Chemstrand Corpn. *USP* 2,816,875

N-Acetyl morpholine,



is a non-hazardous, non-corrosive and non-degrading solvent for linear polyamides. C.O.C.

Stable Aqueous Titania Monohydrate Dispersions for imparting Soil Resistance to Textiles
American Cyanamid Co. *USP* 2,819,174

An aqueous titania hydrate slurry is brought to pH 7·0–7·2, filtered and the filter cake washed with water to remove any sulphate ions. The cake is then re-slurried in water and brought to pH < 5. The dispersion is then treated with an organic amine to bring it to pH > 5, preferably to 7·0–9·5.

USP 2,819,176

To bring the dispersion to pH > 5 a mixture of ammonia and a water-soluble aliphatic or polybasic inorganic acid, e.g. citric, phosphoric, or sulphuric acid, is used. This yields a dispersion of average particle size < 0·1 μ.

USP 2,819,177

To bring the dispersion to pH > 5 a mixture of a water-soluble aliphatic or polybasic inorganic acid and an alkali metal hydroxide, phosphate, borate, or carbonate, is used. C.O.C.

Epoxy Resins and Polyalkyleneimines for Reducing the Felting Properties of Wool (X p. 882)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Nitration of 2-Nitro-4-bromobenzoic Acid
H. Goldstein and S. Mohanna

Helv. chim. Acta, **41**, 470–473 (March 1958)

The nitration of the title substance with HNO_3 (sp.gr. 1·52) in conc. H_2SO_4 gives mainly 2:5-dinitro-4-bromobenzoic acid together with a small amount of the isomeric 2:3-dinitro-4-bromobenzoic acid. H.H.H.

Reaction and Structural Rearrangements of Nitro Derivatives. II—Intermediate Products in the Reaction of o-Nitrophenol Dyes
I. Matei and E. Cocea

Acad. rep. populare Romîne, Studii cercetări chim., **5**, 241–51 (1957): *Chem. Abs.*, **52**, 9042 (10 June 1958)

o-Nitrophenol dissolved in $H_2SO_4{\cdot}H_2O$ and treated with varying amounts of 20% oleum and S gives the following products. At $< 2°$c., 2:2′:4:4′-tetrahydroxy-5:5′-dinitrosodiphenyl-3:3′-disulphonic acid; the Ca salt, with $5H_2O$, is golden-yellow; Ba salt, $3H_2O$, copper-red. At 125–130°c., 2:2′:3:4:4′-pentahydroxy-5-amino-5′-hydroxylaminodiphenylsulphonic acid. At 135–140°c. (3 hr.), 2:2′:3:3′:4:4′-hexahydroxy-5-hydroxylamino-5′-nitrosodiphenyl. E.T.

Quantitative Treatment of Substituent Effects in the Naphthalene System
P. R. Wells and E. R. Ward

Chem. and Ind., 528–529 (3 May 1958)

Using existing reaction rate and equilibrium data, a series of numbers (σ) expressing substituent effects have been calculated for comparison with conclusions arrived at from new experimental results (cf. Ward *et al.*, *J.C.S.*, 2974 (1954); 1979 (1956); 2634 and 4816 (1957)), especially with regard to their transmission in the naphthalene system. It is found that: (i) in reactions of phenols and naphthylamines, the 4*a*-nitro group requires a much higher σ-value than it requires in the other reactions, which parallels the requirements of the *p*-nitro-group in reactions of phenols and anilines; (ii) the σ values for chloro- and bromo-substituents are very similar; (iii) certain positions have similar σ values, e.g. 5*a*-7*a*, 5β-7β, 8β-6β, and, in particular, 4β-3*a* which formally resemble the *meta*-positions in benzene; (iv) σ values for nitro-substituents in the second ring are not much smaller than those for substituents in the ring containing the reacting side chain. This indicates a considerable transmission of polar effects across the naphthalene system as found experimentally by Ward *et al.* (cf. above). Data by Branch and Calvin and by Veselý and Jakes are in agreement. H.H.H.

One Hundred Years of Diazo Compounds—Their Impact and Importance in the Chemical Industry
W. H. Cliffe

Chem. and Ind., **39**, 1248–1255 (27 Sept. 1958)

Orientation by Electrophilic Aromatic Substitution: General Base Catalysis as an Additional Orientation Factor. Multicentred (Concerted) Mechanism in o-Phenol Couplings
O. A. Stamm and H. Zollinger

Helv. chim. Acta, **40**, 1955–1978 (Oct. 1957)

The azo coupling reaction of *o*-nitrodiazobenzene with 1-naphthol-3-sulphonic acid yields a mixture of the 2- and 4-azo-deriv., and the *o*/*p*-ratio can be varied within wide limits by temp. and buffer comp. of the reaction medium. Both reactions are subject also to general base catalysis, which is now found to be an additional factor influencing orientation. In 1-naphthol-3-sulphonic acid (I) the reaction in 4-position is catalysed more effectively by bases than the ortho-reaction, and is explained by inductive and steric effects in the intermediate of the substitution; a similar explanation holds for the comparison of the *o*-reaction of 1-naphthol- and 1-naphthylamino-3-sulphonic acid. Water (as a base) is more effective in the *o*-reaction of (I) than in its *p*-reaction. It is concluded that the cause is a concerted mechanism of proton transfer from carbon atom 2 *via* one mol. of water to the phenolic oxygen. The extremely large difference in activation entropy of 28 kcal./degree between the *o*- and *p*-reaction is probably, in part, a consequence of the different mechanism of proton loss in *o*- and *p*-coupling (concerted and classical mechanism respectively). H.H.H.

Polarographic Reduction of Diazotised Aromatic Amines
R. M. Elofson

Canadian J. Chem., **36**, 1207–1210 (Aug. 1958)

The overall reaction of diazotised aromatic amines at a dropping Hg electrode involves a 4-electron reduction. The first wave in the polarographic reduction is due to an adsorption phenomenon resulting from the 1-electron reduction to a free radical (which is stabilised at the Hg electrode) according to—

$$ArN_2^+ + e \rightarrow ArN_2$$

The stability of the adsorption complex is the principal factor which determines the potential at which the adsorption current occurs. The half-wave potential should be correlated with the adsorptivities of the free radicals on the Hg electrode at various potentials. J.W.D.

Pyridine-Cuprous Chloride Complex as Catalyst for Autoxidation. I—Preparation of Azo Compounds from Primary Aromatic Amines
A. P. Terent'ev and Ya. D. Mogilyanskiĭ

J. Gen. Chem. U.S.S.R., **28**, 1959–1962 (July 1958)

Primary amines in pyridine soln. in the presence of Cu_2Cl_2 and molecular oxygen undergo oxidation to azo compounds. It is shown that $Cu_2Cl_2{\cdot}6Py$ is the catalyst for this reaction. It is impossible to replace Cu_2Cl_2 by other salts, even those of copper; similarly, replacement of pyridine by other solvents, e.g. alcohol, dioxane, toluene, dichlorethane, or quinoline does not yield successful catalyst. A stream of pure oxygen at room temp. gives the most satisfactory results. This reaction is of use for the preparation of symmetrical azo compounds, e.g. *p*-azotoluene, *pp*′-dimethoxyazobenzene, etc. G.J.K.

Halogen Replacement in Azo Compounds

I—Replacement of Chlorine in 2-Chlorophenylazo-2′-naphthol by an Alkoxy Group
B. I. Stepanov, M. A. Salivon, V. F. Lagidze, and L. A. Dedyukhina

J. Gen. Chem. U.S.S.R., **28**, 1915–1921 (July 1958)

The interaction of Na-alcoholate with azo dyes, obtained from *o*-chloraniline and β-naphthol allows replacement of the chlorine atom by an alkoxyl group (OR, where R = CH_3, C_2H_5, *n*-C_4H_9, *iso*-C_5H_{11}, *n*-C_6H_{13}, *n*-C_8H_{17}, or *n*-$C_{18}H_{37}$). The reaction occurs under mild conditions and is facilitated by the presence of Cu salts. Reductive splitting of the alkoxy-azo dye yields the corresponding *o*-alkoxy-aniline.

II—Reaction of 2-Chlorobenzeneazo-2′-naphthol with Phenolates
B. I. Stepanov, L. A. Dedyukhina, and T. T. Strashnova

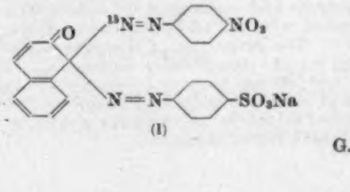
Ibid., 1921–1925

The interaction of Na-phenolate (from phenol; *o*-, *m*- and *p*-cresol; 3:5- and 2:4-xylenol; and similar derivatives) with azo dyes obtained from *o*-chloraniline and β-naphthol allows replacement of the chlorine atom by the aryloxy group. This reaction is carried out in aq. alkaline media in the presence of Cu salts, under which conditions very little replacement of Cl by OH occurs. Reductive splitting of these aryloxy substituted azo dyes produces the corresponding *o*-aryloxy anilines. G.J.K.

Investigation of the Mechanism of Diazo Exchange in Azo Dyes of the Naphthalene Series using Labelled Nitrogen
B. A. Geller

J. Gen. Chem. U.S.S.R., **28**, 1944–1950 (July 1958)

The reaction between *p*-benzenesulphonic acid-azo-β-naphthol and *p*-nitrobenzene-diazonium hydroxide has been used to study the mechanism of diazo exchange. The results obtained by means of ^{15}N (originally in the nitrous acid used to diazotise *p*-nitroaniline) support the mechanism of the electrophilic substitution. An *ortho*-naphthoquinonyl structure (I) is suggested as intermediate—



(I)

G.J.K.

Interaction of Diazo Compounds with Sulphamic Acid and its Derivatives. X—Coloured Salts of Acylamino-aryl-sulphonic Acids with Diazonium Bases
D. Z. Zavel'skiĭ and L. A. Lishnevskaya

J. Gen. Chem. U.S.S.R., **28**, 1925–1930 (July 1958)

It is established that the coloured products of the interaction of diazonium salts with acylamino-aryl-sulphonic acids (G. Schroeter, *Ber.*, **39**, 1559 (1906)) are true diazonium salts. The deepening of the colour of the latter salts is enhanced by (1) increasing electrophilic character of the substituent in the aryl nucleus of the diazo moiety, (2) decreasing acidic nature of the acyl group, (3) the increase in the number of condensed benzene rings in the aryl portion of the acylamino-arylsulphonic acid system. The colour is explained on the basis of a "special" type of salt linkage. G.J.K.

Physical Properties of the Aminoazobenzene Dyes. IX—Absorption Spectra in Alcohol and Acid Solution of Disazobenzene Dyes
E. Sawicki

J. Org. Chem., **23**, 532–5 (1958):
Chem. Abs., **52**, 14324 (10 Sept. 1958)

Spectral evidence obtained during investigation of the function of proton addition and the absorption spectra in various solvents of 4-dimethylamine-*p*-disazobenzene dyes indicates that the first proton added to the β-azo *N* and the second proton to the δ-azo *N*. Syntheses of a number of these dyes are given. C.O.C.

Constitution and Colour of Formazones
H. Ziegler

Mededeel. Vlaam. Chem. Ver., **20**, (1), 1–11 (1958):
Chem. Abs., **52**, 13420 (25 Aug. 1958)

A discussion of the relationship between the colour and the chemical constitution of the formazones. Colour is governed by the central azohydrazoic ring, which has a resonance effect and alternate polarisation of the atoms in the central ring. Alteration in colour following the inversion law of auxochromes results from substitutions in the central ring. Hypsochromic or bathochromic effects result if electron acceptors or donors are bound to positive or negative polarised atoms respectively. The effect on colour by chelation with metals or constitutional modifications on the *meso* C atom or on the two negative polarised N atoms is also discussed. C.O.C.

Metachromism and Formation of a Reversible Complex between Acridine Orange (C.I. 46005) and Heparin
W. Appel and V. Zankev

Z. Naturforsch, **136**, 126–134 (1958);
Chem. Abs., **52**, 14326 (10 Sept. 1958)

When heparin is added to a 10^{-5}M solution of C.I. 46005 a metachromatic shift in the absorption maximum of the dye occurs. The amount of shift is directly related to the heparin concentration in the range of 0·1–0·5 I.V. per mol. Spectrophotometric evidence indicates that 40–50 molecules of dye are bound to each heparin molecule. Addition of NaCl greatly reduces the metachroism because the dye cations on the negatively charged heparin molecule are replaced by Na ions. When the dye concentration is increased to 10^{-4}M the heparin-dye complex begins to precipitate. The major effects at this concentration are caused by weak association of the dye molecules. C.O.C.

Relationship between Structure and Colour of Organic Compounds. VIII—Indicator Properties of Some Arylhydrazones of 9-Acridinecarboxaldehyde
A. A. Kharkharov

Vestnik Leningrad. Univ., **12**, (22), *Ser. Fiz. i Khim.* (4), 169–172 (1957):
Chem. Abs., **52**, 13521 (25 Aug. 1958)

Arylhydrazones of 9-acridinecarboxaldehyde gain a proton and transform yellow or orange to red or green salts in the pH range 2–6. By using twelve compounds with substituents such as CH_3 or OCH_3 on the phenyl but no COOH, sulpho or nitro, silk and wool are dyed blue or violet, while acetate rayon and polyamide fibres are dyed yellow or brown or orange. Evidently the salts formed must have added a proton on the acridine ring N atom and not on the hydrazone N atoms. C.O.C.

Azo Dyes derived from Luminol
R. Pařízek and V. Moučka

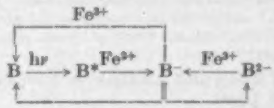
Chem. Průmysl, **7**, 651–2 (1957)

Preparation of several monoazo dyes derived from Luminol is described, they are chemiluminescent. Their properties and possible uses are discussed. C.O.C.

Photoreduction of Methylene Blue (C.I. Basic Blue 9) and Thionine (C.I. Basic Blue 25) by Ferrous Sulphate using Flash Irradiation
C. A. Parker

Nature, **182**, 245–246 (26 July 1958)

The results of flash irradiation studies of acidic soln. of Methylene Blue (B) and $FeSO_4$ can be interpreted in terms of the scheme—



The equilibrium concn. of semiquinone (B^-) appears to be lower than previously thought. Thionine behaves similarly and studies of the fluorescence quenching indicate that the semiquinone is formed from a triplet state and not an excited singlet state. A.J.

Sulphenic and Selenenic Acids and their Derivatives V—Anthraquinone-1:4-disulphenic and -1:4-diselenenic Acids
W. Jenny

Helv. chim. Acta, **41**, 317–326 (March, 1958)

The syntheses of the title substances are described starting from 1:4-dithiocyano- and 1:4-diselenocyano-anthraquinone as initial substances respectively, and the optical properties of their anions are reported. It is found that anthraquinone-1:4-diselenenylacetate exhibits an abnormally large resistance towards alcohols. Potassium thiocyanate is found to give 1-nitro-2:5-dithiocyanobenzene with diazotised 3:4-dinitroaniline.

VI—Synthesis of Anthraquinone-1:5-disulphenic Acid
W. Jenny

Ibid., 326–331

The synthesis of the title substance from 1:5-dithiocyanoanthraquinone and the optical properties of its anion are described. Based upon the great similarity of the spectra of anthraquinone-1-sulphenic acid and its methyl ester, the conclusion is drawn that free sulphenic acids and their esters possess identical structures.

VII—New Methods for the Preparation of Selenenic Acid Esters
G. Hölzle and W. Jenny

Ibid., 331–338

The reaction of selenocyanides with alcohols in the presence of certain metallic salts such as silver acetate or carbonate or copper acetate, gives the respective selenenic acid ester directly. The reaction does not occur with the thiocyanates which, instead, afford the silver salts of the thiols. 2-Nitrobenzeneselenenyl bromide reacts with methanol in the presence of silver acetate to give 2-nitrobenzeneselenenic acid methyl ester and not 2-nitrobenzeneselenenyl acetate as stated by Behaghel and Müller (*Ber.*, **68**, 1540 (1935)).

VIII—Photocatalytic Bromination of the Selenocyanides
G. Hölzle and W. Jenny

Ibid., 356–360

It is established that the reaction of diselenides and of selenocyanides with bromine is accelerated by ultraviolet light, and that selenocyanides, which will not react with bromine in diffused daylight, are converted directly into selenenyl bromides when irradiated with the above. The reaction does not occur with thiocyanates. The mechanism of the bromination of selenocyanides is discussed. H.H.H.

Reductions with $LiAlH_4$ in the Isatin Series. I—Preparation and Properties of 3-Hydroxyindoline
E. Giovannini and T. Lorenz

Helv. chim. Acta, **40**, 1553–1561 (Oct. 1957)

It is shown that $LiAlH_4$ can reduce isatin to 3-hydroxyindoline (I), indole, indigo, and indirubin. Details are given for the preparation of I and of its properties. H.H.H.

Physicochemical and Colloidal Properties of Sols of Some Pigments used in the Mass Coloration of Viscose
S. P. Varova and E. M. Aleksandrova
Trudy Moskov. Khim.-Tekhnol. Inst. im. D.I. Mendeleeva, (25), 11–16 (1957)

A method is described of preparing fine particle sized powders and sols of "Blood-Red 2C" and phthalocyanine blues for the mass coloration of viscose. An optical absorption method is given for determining the chemical stability of pigments intended for this purpose. The factors affecting the aggregate stability of pigment sols in presence of large amount of anion-active substances were studied. Two of the pigments were coagulated in the viscose by various ionic electrolytes, NaCl, $BaCl_2$, NaOH, Na_2S, $MgCl_2$. Anion-active compounds and the viscose exert a stabilising effect. Drying of the pigments exerts a negative effect. C.O.C.

Influence of Acids and Alkalies on Absorption Spectra of Pyridine Dyes
N. E. Grigor'eva, I. K. Gintse, and A. P. Severina
J. Gen. Chem. U.S.S.R., **26**, 3447–3455 (1956): *Chem. Abs.*, **52**, 14326 (10 Sept. 1958)

English translation of article previously abstracted, J.S.D.C., **73**, 272 (1957). C.O.C.

Analysis of Structural Effects on the Spectrum. I—Comparative Study of Phenomena of Colour in Azomethins
V. A. Izmail'skii and E. A. Smirnov
J. Gen. Chem. U.S.S.R., **26**, 3389–3406 (1956): *Chem. Abs.*, **52**, 14326 (10 Sept. 1958)

English translation of article previously abstracted, see J.S.D.C., **73**, 272 (1957). C.O.C.

Toxic and Non-toxic Dyes for Food
H. Druckrey
Z. Krebsforsch., **60**, 344–360 (1955): *Chem. Abs.*, **52**, 14881 (10 Sept. 1958)

Review with numerous references. C.O.C.

Status of the Dye Industry in Poland
F. Kacprzak
Chemik (Gliwice), **11**, 179–183 (1958): *Chem. Abs.*, **52**, 15071 (10 Sept. 1958)

Review. C.O.C.

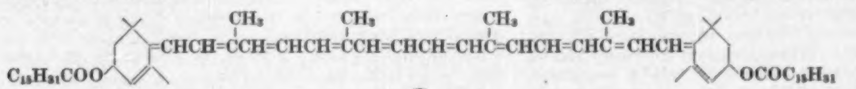
Carotenoid Syntheses

XX—Optically Active α-Carotenes
C. Tscharner, C. H. Eugster, and P. Karrer
Helv. chim. Acta, **40**, 1676–1677 (Oct. 1957)

The hitherto unknown *l*-α-carotene has been isolated by a similar procedure to that employed previously (cf. *ibid.*, **33**, 1952 (1950) and **38**, 610 (1955)) for the synthesis of *d,l*-α-carotene.

XXI—Ash Wood Xanthin
R. Entschel and P. Karrer
Ibid., 1809–1811

Physalien (the dipalmitic acid ester of zeaxanthin) when dehydrogenated by means of bromosuccinimide gives the dipalmitate (I) of ash wood xanthin which saponifies to the xanthin. This synthetic product is identical with the natural derivative.



(I)

XXII—Reaction Products of β-Carotene with Bromosuccinimide. (Introduction of Ethoxy and Hydroxyl Groups into Hydrocarbons)
R. Entschel and P. Karrer
Ibid., **41**, 402–413 (March 1958)

Rapid reaction of bromosuccinimide (I) with β-carotin (II) in presence of an alcohol (C_2H_5OH, CH_3OH) and subsequent treatment of the reaction product with strong bases (*N*-ethylmorpholine, *N*-ethylpiperidine, etc.) gives 4-ethoxy- and 4:4′-diethoxy-β-carotin with C_2H_5OH (or 4-methoxy and 4:4′-dimethoxy-β-carotin with CH_3OH), 4-keto-4′-ethoxy- (or methoxy)-β-carotin, 4:4′-diketo-β-carotin, and retro-dehydrocarotin. When I is treated with II in the presence of glacial acetic acid and the acid formed is neutralised, 4:4′-dihydroxy-β-carotin ester is given in good yield and saponifies to 4:4′-dihydroxy-β-carotin. The mechanism of these reactions is discussed H.H.H.

***cis*-Forms of Canthaxanthin**
C. Gansser and L. Zechmeister
Helv. chim. Acta, **40**, 1757–1767 (Oct. 1957)

Thermal and photochemical treatments are described for the conversion of the fungal carotenoid canthaxanthin, $C_{40}H_{52}O_2$ (4:4′-diketo-β-carotene) into a stereoisomeric mixture which resolves chromatographically into six *cis*-forms termed "neo-canthaxanthins A–F". Of these A–C were obtained in crystalline form, while C proved to be identical with the central-mono*cis*-canthaxanthin synthesised by Isler *et al.* (*Verh. Naturf. Ges. Basel*, **67**, 379 (1956)). Spectra data are included and some tentative configurational assignments proposed. H.H.H.

New Carotenoid, Monohydroxy-α-carotene (Fisoxanthine)
C. Bodea and E. Nicoara
Acad. rep. populare Romîne, Filiala Cluj, Studii cercetări chim., **7**, 133–9 (1956): *Chem. Abs.*, **52**, 12810 (10 Aug. 1958)

α-Carotene (C.I. 75130) (80 mg.) in 2000 ml. was acidified with 0·1N-H_2SO_4 (4 ml.). The solution was divided into 100 ml. portions and allowed to autoxidise for 20 days. They were then mixed together, quenched with water and extracted with petroleum ether. The ether layer was washed, dried and then chromatographed over a column of MgO and fine sand. The zone containing monohydroxy-α-carotene (fisoxanthine) was extracted with a mixture of equal parts of alcohol and petroleum ether. The petroleum ether was evaporated off and the alcohol portion cooled at 0°C. to give 10 mg. of fisoxanthine. C.O.C.

Chloroplast Pigments and Chromatographic Analysis
H. H. Strain
Ann. Priestley Lectures (1958), 180 pp.: *Chem. Abs.*, **52**, 13890 (25 Aug. 1958)

An account of investigations into the chloroplast pigments of a large number of plants. Appendices give qualitative data on more than 450 species including flowering plants, ferns, mosses, algae and others. The various pigments were separated by chromatography. Absorption spectra for the following pigments are given: rhodoxanthin, a xanthophyll from green algae, siphonaxanthin, siphonein, fucoxanthin, neosiphonaxanthin, neosiphonein, xanthophylls from *Protosiphon*, axanthophyll from *Ankistrodesmus*, xanthophylls and carotene from *Euglena*, xanthophylls from *Heterokontae*, myxoanthophyll and myxoxanthin. 69 references. C.O.C.

Synthetic Mica (C.I. Pigment White 20) and Synthetic Asbestos
T. Noda
Kôgyô Kagaku Zasshi, **59**, 1266–1271 (1956): *Chem. Abs.*, **52**, 14445 (10 Sept. 1958)

Review of the structure, properties and synthesis of artificial mica and asbestos. 68 references. C.O.C.

PATENTS

15:15′-Dehydrocryptoxanthine and its Esters
F. Hoffmann–La Roche & Co. *BP* 802,570

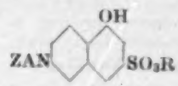
Acetylene is bilaterally condensed in an organo-metal condensation with 8-[2′:6′:6′-trimethyl*cyclo*hexen-(1′)-yl]-2:6-dimethyl-octatrien-(2:4:6)-al-(1) or 8[2-′:6′:6′-trimethyl*cyclo*hexylidene]-2:6-dimethyl-octatrien-(2:4:6)-al-(1) on the one side and with an 8-[2′:6′:6′-trimethyl*cyclo*hexen-(1′)-yl]-2:6-dimethyloctatrien-(2:4:6)-al-(1) or 8-[2′:6′:6′-trimethyl*cyclo*hexylidene]-2:6-dimethyloctatrien-(2:4:6)-al-(1) containing OH or esterified OH in the 4′-position. The resultant condensate, after esterification if necessary, is subjected to elimination of 2 mol. of water or acid and allyl rearrangement and, if necessary, the product hydrolysed with alkali. C.O.C.

Carotenoid Food Dyes
F. Hoffmann–La Roche & Co. *BP* 803,077

≮ 3% of a carotenoid pigment, e.g. β-carotene (C.I. Natural Yellow 26) dissolved in a solvent which is solid at ordinary temperatures, e.g. cetyl palmitate or glyceryl monostearate, does not tend to crystallise out during prolonged storage and so when used as a food dye yields uniform coloration and no tendency for specking. C.O.C.

Azine Cyan Colour Formers
General Aniline *BP* 802,553

Compounds of formula—



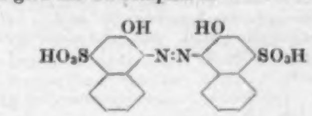
(A = subst. or unsubst. benzyl; Z = subst. or unsubst. benzyl, phenyl, or naphthyl; R = H or a salt-forming group), e.g. 6-[(*N*-*p*-Nitrobenzyl, *N*-benzyl)amino]-1-naphthol-3-sulphonic acid are photographic colour formers fast to diffusion. When used in conjunction with a 2:4-diamino aniline developer they yield brilliant cyan azine dyes having high green transmission. C.O.C.

Synthesis of Carotenoids
F. Hoffmann-La Roche & Co. *BP* 802,136

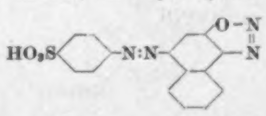
β-Carotene (C.I. 75130), 3:4:3′:4′-bisdehydro-β-carotene, zeaxanthine, lycopene (C.I. 75125) and their 15:15′-dehydro analogues are manufactured in the following stages. A 3:8-dimethyl-2:9-dialkoxy-decapentane-(1:3:5:7:9) or the correspondingly substituted decatetraen-(1:3:7:9)-yne-(5) are bilaterally condensed in presence of an acidic condensing agent with a 1:1-dialkoxy-2-methyl-4-substituted-butene-(2) in which the substituent is 2:6:6-trimethyl-*cyclo*hexylidene (which may be substituted by an oxo, hydroxy or acyloxy group in the 4-position) or 2:6:6:-trimethyl*cyclo*hexen-(1)-yl (which may be substituted by a hydroxy or acyloxy group in the 4-position) or 2:6:6-trimethyl*cyclo*hexadiene-(1:3)-yl or 2:6:6-trimethylhexen-(5)-ylidene. The resulting 1:18-disubstituted 3:7:12:16-tetramethyl-4:6:6:13:13:15-hexaalkoxyoctadecapentane-(2:7:9:11:16) or correspondingly substituted octadecatetraen-(2:7:11:16)-yne-(9) is hydrolysed in presence of acid. The 1:18-disubstituted-3:7:12:16-tetramethyloctadecaheptane-(2:4:7:9:11:14:16)-dione-(6:13) or the correspondingly substituted octadecahexaen-(2:4:7:11:14:16)-yne-(9)-dione-(6:13) so obtained is reduced to give the corresponding 6:13-diol and, if desired, acylated. This is then treated with aqueous or an hydrous hydrohalic acid to yield a carotenoid. When a 3:8-dimethyl-2:9-dialkoxydecatetraen-(1:3:7:9)-yne-(5) is used as one of the starting materials the final product is a 15:15′-dehydrocarotenoid which can be partially hydrogenated at the triple bond and isomerised to give the same product as if a 3:8-dimethyl-2:9-dialkoxydecapentaene-(1:3:5:7:9) had been one of the starting materials. C.O.C.

Metal(Copper)-complex Azo Compounds—Intermediates and Direct Dyes
FBy *BP* 802,098

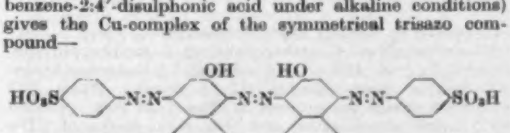
Symmetrical copper-complex azo compounds are made by treating *o*-hydroxydiazonaphthalene compounds with aq. ammoniacal cuprous salts. Thus 1-diazo-2-naphthol-4-sulphonic acid is treated at room temperature with a solution obtained by adding hydroxylamine to ammoniacal $CuSO_4$, to give the Cu complex of—



In a similar manner, the *o*-hydroxydiazo compound—



(obtained by oxidising 1-diazonaphthalene-4:1′-azobenzene-2:4′-disulphonic acid under alkaline conditions) gives the Cu-complex of the symmetrical trisazo compound—



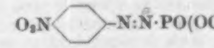
which dyes cotton green. E.S.

15:15′-Dehydro-zeaxanthin and its Esters
F. Hoffmann-La Roche & Co. *BP* 802,569

Acetylene is bilaterally condensed in an organo-metallic condensation with an 8-R[1]-2:6-dimethyloctatrien-(2:4:6)-al-1 (R[1] = 2:6:6-trimethyl*cyclo*hexen-(1)-yl or 2:6:6-trimethyl*cyclo*hexylidene containing OH or esterified hydroxy in the 4-position). The diol so obtained is then converted into the 15:15′-dehydro-zeaxanthine or an acyl derivative thereof by subjecting it after esterification if necessary to the elimination of 2 mol. of water or acid and simultaneous allyl rearrangement and, if necessary, hydrolysing the product. Thus 4′-acetoxy β-C_{19} aldehyde (prepared by the process of *BP* 802,568) in absolute benzene is stirred with a suspension of acetylene-di(MgBr) in absolute ether for 3 hr. at 60°c. It is then passed into ice water containing a little H_2SO_4 and extracted with ether. The extract is washed with dil. Na_2CO_3 and water, dried with Na_2SO_4 and evaporated. The residue is dissolved in methylene chloride, acetic and hydrobromic acids added at −40°c., the mixture stirred for 90 sec. at −35°c., diluted with water and stirred for 3 hr. at 0°c. It is then washed with dil. Na_2CO_3 and water, dried with Na_2SO_4 and evaporated. The residue is 3:3′-diacetoxy-15:15′-dehydro-zeaxanthine which can be hydrolysed to yield 15:15′-dehydro-zeaxanthine. C.O.C.

Azophosphonic Acid Esters
FBy *BP* 802,198

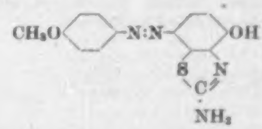
Azophosphonic acid esters Aryl·N:N·PO(OAlk)$_2$ are prepared by condensing diazo compounds with dialkyl phosphites. They do not show a diazo reaction towards coupling compounds, and are thermally comparatively stable. They may be used as intermediates for dyes or for the preparation of arylhydrazines. Thus diazotised *p*-nitroaniline is stirred with an aq. solution of dimethyl phosphite, whilst neutralising with $NaHCO_3$, to give—



which is a red compound, insoluble in water but soluble in organic solvents. E.S.

Yellow, Metallisable Monoazo Disperse Dyes from 4-Hydroxybenzthiazoles
ICI *BP* 801,900

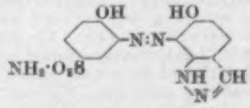
Diazotised aniline, which may carry nuclear substituents, e.g. CF_3, CH_3, Hal, $SO_2{\cdot}NH_2$, is coupled with 4-hydroxybenzthiazole, which may be substituted in the 2-position by Cl, phenyl, NH_2, or acetylamino, to give yellow disperse dyes which may be metallised, especially with Cu compounds, on the fibre. Thus diazotised *p*-anisidine is coupled with 2-amino-4-hydroxybenzthiazole in presence of NaOH, Na_2CO_3 and β-ethoxyethanol to give—



which after grinding with a dispersing agent dyes cellulose acetate and nylon yellow when aftercoppered with $CuCl_2$ or the Cu complex of ethylenediamine. E.S.

Metal(Chromium and Cobalt)-complex Monoazo Dyes for Wool, etc. having an Indazole Residue
Fran *BP* 802,076

o-Aminophenol, or anthranilic acid, or derivatives of them free from SO_3H or COOH groups, are diazotised and coupled with 5(or 6)-hydroxyindazole, and the products converted into Cr or Co complexes which dye wool, nylon, etc. from neutral or weakly acid baths. Thus, 2-aminophenol-4-sulphonamide is diazotised and coupled with 6-hydroxyindazole to give—

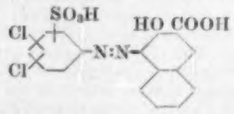


Boiling with aq. sodium chromo-tartrate at a pH of ca. 11 gives a violet dye for wool. E.S.

Maroon Monoazo Pigments

American Cyanamid Co. *USP* 2,821,525

Monoazo compounds—

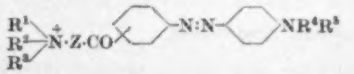


are converted into lakes with salts of divalent metals to give maroon pigments of good fastness. Thus *o*-dichlorobenzene is nitrated, and the mononitro compound reduced and sulphonated to give a mixture of dichloroaniline-sulphonic acids, the predominant isomer being 3:4-dichloroaniline-6-sulphonic acid (I). This mixture is diazotised and coupled with 3-hydroxy-2-naphthoic acid in presence of $MnCl_2$. By using substantially pure I instead of the mixture of amines the resulting Mn lake is lighter in mass tone and faster to light. E.S.

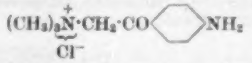
Monoazo Basic Dyes for Polyacrylonitrile Fibres

DuP *USP* 2,821,526

Monoazo dyes—



(R^1 = Alk; R^2 = Alk or hydroxyalkyl; R^3 = Alk, hydroxyalkyl or aralkyl; or R^1, R^2, R^3 with N may be a heterocyclic ring; Z = alkylene of 1–3 C; R^4, R^5 = H, Alk, or cyanoethyl, but R^4 may be phenyl; the $R^1R^2R^3N{\cdot}Z{\cdot}CO$ group is in the *m*- or *p*-position to the azo link; the benzene nuclei may contain Alk or Hal as substituents) are orange to red-violet basic dyes for polyacrylonitrile fibres. Thus acetanilide and chloroacetyl chloride are condensed in presence of $AlCl_3$ to give *p*-acetamidophenacyl chloride, which after stirring with trimethylamine and hydrolysis of the acetamido group with aq. HCl gives *p*-aminophenacyl-trimethylammonium chloride—

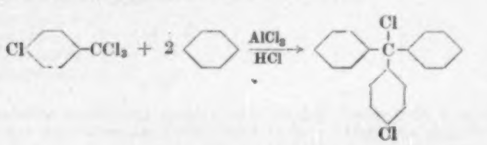


This is diazotised and coupled with *m*-chloro-*N*:*N*-diethylaniline to give a red-orange. E.S.

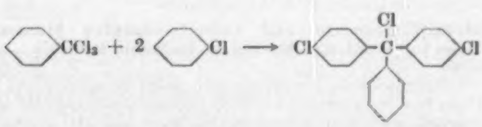
Amino-Triaryl-Carbinols and Triarylmethane Dyes

Ciba *BP* 800,857

Amino-triaryl-carbinols are made by reacting a triaryl-carbinol, in which at least one aryl group contains a para-halogen atom, with NH_3 or a primary arylamine, e.g. 1-aminonaphthalene, aniline. The triaryl-carbinol starting materials may be obtained as follows—



or



Suitable quantities for such reactions are 1 mol. aryltrihalogen methane, 2 mol. halogenobenzene, 1·5 mol. $AlCl_3$, and 1% by wt. of HCl on the wt. of $AlCl_3$ at 80–100°C. Replacement of the halogen by amino follows; thus, tri-(*p*-chlorophenyl)-carbinol (182), Cu pdr. (2), $CuSO_4$ cryst. (10), 25% ammonia (600 by vol.) are heated in an autoclave at 195–200°C. for 10–12 hr. The resinous product is dissolved in 20% H_2SO_4 (2000), purified with activated C and the *p*-chlorophenyl-di-(*p*-aminophenyl)-carbinol is precipitated by adding ammonia. The corresponding triarylmethane dye is obtained from this carbinol and HCl and dyes bordeaux shades on polyacrylonitrile fibres from an acid bath. E.T.

Yellow Anthraquinone Monoazo Pigments

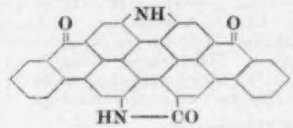
General Aniline *USP* 2,820,787

2-Amino-3-halogenoanthraquinones are diazotised and coupled with acetoacet-2:4-dialkylanilines to give yellow pigments. The preferred product is 2-amino-3-chloroanthraquinone→acetoacet-2:4-xylidide. E.S.

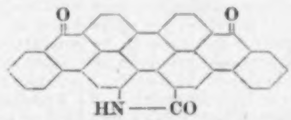
Black Dibenzanthrone Vat Dye

General Aniline *USP* 2,819,270

A black vat dye of high light fastness is of formula—

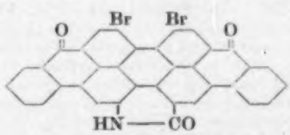


It is made from aminodibenzanthrone (aminoviolanthrone) which is obtained by nitration of dibenzanthrone followed by reduction (ref. Centralblatt, 1929; II 496 & *FP* 651,152). Thus, nitrobenzene (640), aminodibenzanthrone (62·8) and chloroethyl carbonate (63·6) are stirred 2 hr. at 90–95°C., 2 hr. at 130–5°C. and 2 hr. at 170–5°C. Cooling and filtration yield—



93% theory

This (29·9), iodine (3), and nitrobenzene (450) are heated to 155–60°C., Br_2 (12·3) in nitrobenzene (60) is added and stirred 4 hr. at 155–60°C. The product separated by filtration is—



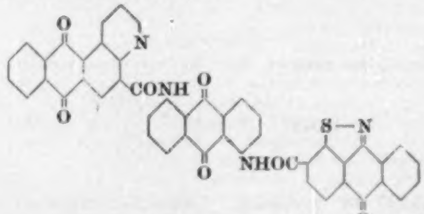
83% theory

The dibromo compound (24), 28% aq. ammonia (360) and $CuSO_4$ crystals (3) are then autoclaved 10 hr. at 200°C., filtered and the final product (88% theory) is washed neutral and dried. E.T.

Yellow Anthraquinone Vat Dyes

FBy *BP* 801,687

Greenish-yellow vat dyes of very high light fastness are made by reacting a 1-acylamino-5-amino-anthraquinone, whose acyl radical is derived from a quinoline-8-carboxylic acid (ref. *BP* 800,962, J.S.D.C., **74**, 792 (Nov. 1958)) with acylating agents which are either (*a*) aliphatic or aromatic dicarboxylic acids, or (*b*) yellow vattable heterocyclic carboxylic acids containing N in the heterocyclic ring. Examples of (*b*) are 1:9-thiazolanthrone-2-carboxylic acid; 1:2-thiazolo-anthraquinone-3-carboxylic acid; 1:2-imidazole-anthraquinone-3-carboxylic acid; 1:9-pyrazolanthrone-2-carboxylic acid and 1:9-anthrapyrimidine-2-carboxylic acid. The dye—



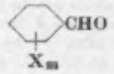
is prepared by heating nitrobenzene (600 cc.) and 1-(5′:6′:phthalylquinoline-8′-carbonylamino)-5-aminoanthraquinone (20 g.) at 130°C. and adding 1:9-thiazolanthrone-2-carboxylic acid chloride (12 g.) slowly. When HCl evolution ceases the product is filtered at 90°C., washed with warm nitrobenzene and then with methanol. The dyes disclosed in this patent have superior properties to the similar dyes described in *GP* 579,325 and 696,423. E.T.

Phthalocyanine-type Colorants
Bergwerksverband zur Verwertung von Schutzrechten der Kohlentechnik *BP* 801,488

Pyromellitic acid (benzene-1:2:4:5-tetracarboxylic acid), or crude mixtures of carboxylic acids containing pyromellitic acid, when heated with urea, a metal or metal salt and a catalyst, e.g. NH_4 phosphovanadate, NH_4 phosphomolybdate, or boric acid, give deep green products similar to phthalocyanines. The crude carboxylic acid mixtures are obtained by oxidation of fuels, e.g. hard coal, with HNO_3. In the "phthalocyanine"-forming reaction urea may be replaced by biuret, guanidine, dicyandiamide or cyanic acid and $CuCl_2$, $MgSO_4$, Ni nitrate or Pb acetate are suitable metal salts. Examples of reaction conditions are 8 hr. at 150°C. or 4 hr. at 200°C. Alternatively, this reaction may be carried out in solvents, e.g. nitrobenzene, di- or tri-chlorobenzenes or diethyleneglycol; the lower-boiling solvents benzene, toluene, chlorobenzene, etc. may be used under pressure. The crude reaction products are purified by leaching with water and/or dil. mineral acid followed by dissolving in ammonia and reprecipitation with acid. The final products are useful in printing pastes, pigments and for colouring paper, plastics, and linoleum. E.T.

Light-sensitive Rhodanine Esters of Maleic Anhydride Copolymers
Eastman Kodak Co. *USP* 2,824,087

Light-sensitive polymeric dyes are obtained by treating maleic anhydride copolymers with 3-ω-hydroxyalkyl-5-substituted rhodanines obtained by treating a 3-ω-hydroxyalkyl rhodanine with a compound of formula—



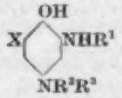
(m = 1 or 2; X = H, OH, Alk of 1–4 C, alkoxy of 1–4 C, dioxymethylene, nitro, acetamino or NRR (R = Alk of 1–4 C), naphthyl, anthryl, or a heterocyclic group), e.g. the reddish-violet 3-(2-hydroxyethyl)-5-(4-dimethylaminobenzylidene)-rhodanine. C.O.C.

Dyed Resinous Pigments
Switzer Brothers *BP* 803,057

Pigments of any desired hue are obtained by dyeing a clear, powdered vinyl resin, especially partially hydrolysed vinyl acetate–vinyl chloride copolymers. When using fluorescent dyes, e.g. Rhodamine B (C.I. Basic Violet 10) use of a metallic soap in the dyebath results in better dyeing and brighter products. C.O.C.

Oxidation Bases for Dyeing Human Hair
Société Monsavon L'Oréal *BP* 802,554

The oxidation bases normally used, e.g. polyamines and/or polyaminophenols, are applied after mixing with H_2O_2. Disadvantages are (1) long duration of treatment and (2) damaging of the hair by H_2O_2. These are overcome by using polyaminophenols of formula—



(R^1, R^2 = H, Alk or hydroxyalk of < 4 C; R^3 = H or hydroxyalk of < 4 C; X = Hal, NH_2, OH, COOH, Alk or alkoxy of < 4 C; *or*, when $\nless 2$ of R^1, R^2, R^3 are H, X = NO_2; *or*, when $\nless 1$ of R^1, R^2, R^3 is other than H, X = H). Such compounds are rapidly oxidised to coloured compounds by air so that H_2O_2 need not be used. They are applied as aq. solutions (of the compounds or their salts) at pH 5–8 and oxidation is complete in 10–15 min. 14 examples are given including 6-nitro-2:4-diaminophenol (dark brown with reddish tinge) and 2-(N-β-hydroxyethyl)-amino-4:6-diaminophenol (light brown with greenish tinge). E.T.

Non-chalking Anatase Titanium Dioxide (C.I. Pigment White 6)
National Lead Co. *USP* 2,817,595

Hydrous TiO_2 is calcined at 900–1100°C. in presence of a little of potassium, barium and phosphorus compounds. The product has good colour and high brightness and little tendency to chalk. C.O.C.

Yellow to Reddish-Yellow Iron Oxide Pigments (C.I. Pigment Yellow 42)
DuP *USP* 2,818,348

Highly transparent pigments are obtained by heating precipitated hydrous ferric oxide in aqueous suspension with a petroleum sulphonic acid or salt, followed by flocculating the highly dispersed pigment by treatment with a water-soluble salt of an organic cationic agent and then filtering, washing and drying. C.O.C.

Composite Lead Phosphate–Lead Silicate Pigments
National Lead Co. *USP* 2,822,285

Composite lead phosphate–lead silicate pigments containing PbO, P_2O_5 and SiO_2 in physicochemical combination do not cause increase in the viscosity of paints on storage. They do increase the resistance of the paint film to blistering caused by moisture in the substrate. C.O.C.

Fibrous Silicon Monoxide Pigment
B. F. Goodrich Co. *USP* 2,823,979–80

Fibrous silicon monoxide is obtained by contacting gaseous silicon monoxide with an inert gas under non-turbulent conditions, preferably under conditions of lamellar flow, and then condensing. A small proportion of the product may be spherical particles. The product is a brown pigment useful as a reinforcing pigment for rubber. C.O.C.

Starch-complex Pigment
R. T. Vanderbilt Co. *USP* 2,824,099

The products obtained by the process described in *USP* 2,573,677 (J.S.D.C., **68**, 223 (1952)) are made especially suitable for use in paper making by treating them with alum so that the final product when dispersed in water has pH 3·5–10·0. Thus the precipitate formed by adding sodium silicate to a dilute aqueous solution of a calcium chloride-starch complex is heated with aluminium sulphate at 130–140°F. C.O.C.

Gelatinised Cellulosic-complex Pigment
R. T. Vanderbilt Co. *USP* 2,823,997

The pigments obtained by the process described in *USP* 2,599,094 (J.S.D.C., **69**, 70 (1953)) are made especially suitable for use in paper making by treating them with alum so that an aqueous dispersion of the final product has pH 4–9. Thus bleached sulphite pulp is swollen with $CaCl_2$ and then a dilute aqueous solution of sodium silicate is stirred in. The precipitated pigment is then slurried at 10% consistency in water with dry alum, filtered and dried. The resultant fibrous pigment forms a pulp-like mass when mixed with water. C.O.C.

Composite Rutile Titanium Dioxide (C.I. Pigment White 6)
National Lead Co. *USP* 2,818,347

An extender, e.g. $BaSO_4$ or $CaSO_4$, is mixed with aqueous Ti sulphate prepared by use of a hydrochloric acid leached ore residue. A composite hydrate is precipitated from the solution and is then washed, dried and calcined. C.O.C.

Increasing the Bulk Density and Degree of Aggregation of Extremely Finely Divided Inorganic Substances
G. L. Flemmert *BP* 802,953

Finely powdered, voluminous non-carbonaceous inorganic substances, e.g. SiO_2 or TiO_2, of particle size 5–300 mμ, are treated with $\ngtr 1$ part by weight of a non-solvent per 10,000 parts of solid and then dried. This leaves a product whose final volume is only 5–50% of the original volume. C.O.C.

V—PAINTS; ENAMELS; INKS

Hiding Power of Pigments in Paint

D. Tough

F.A.T.I.P.E.C. (Fed. assoc. techniciens inds. peintures, vernis, émaux, et encres imprimerie Europe continental) Compt. rend. 3e Congr., Spa 265–278 (1955): *Chem. Abs.*, **52**, 15088 (10 Sept. 1958)

Contrast ratio (C.R.) determined by a Hardy spectrophotometer was compared with the spreading rate at complete visual hiding over a black and white pattern for 36 pigments at weight ratio 15/100 in alkyd resin and for 11 chromate pigments at 60/100 weight ratio. To determine C.R. films were cast on 0·0005 in. cellulose acetate sheet with a 0·003 in. Bird applicator; variation in film thickness was $< 10\%$. The spectral reflectance curve was determined for the coated sheet first backed by a black cavity, then backed by MgO. The curves were integrated by the I.C.I. 30 point equal energy method to give Y_B and Y_W, the visual reflectance over black and white. The C.R., Y_B/Y_W, correlates well with visual hiding power for organic pigments as a class and for chromate pigments as another class; the two classes fall on different curves. C.R. also correlates well with visual hiding power for varying concentration of the same pigment. Length of grinding has little effect on C.R. Opacity is defined as the ability of pigment to scatter light and is contrasted with hiding by light absorption. An index of opacity is the ratio of reflectance over black in the non-absorbing part of the spectral curve to the corresponding reflectance over white. As there is about 5% reflectance in the absorbing regions of the spectrum, the opacity index is calculated as $Y_b/Y_w = (Y_B-5)/(Y_W-5)$. Pigments having low opacity are desirable in polychromatic powder, such as blends with Aluminium flake (C.I. Pigment Metal 1). C.O.C.

Influence of Dispersion on the Colour of Carbon Black Enamels

G. Betant

F.A.T.I.P.E.C. (Fed. assoc. techniciens inds. peintures, vernis, émaux, et encres imprimerie Europe continental) Compt. rend. 3e Congr., Spa 189–194 (1955): *Chem. Abs.*, **52**, 15088 (10 Sept. 1958)

Carbon Black was dispersed in glyceryl phthalate alkyd resin and hydrocarbon solvent in a ball mill. Good colour was got with a maximum 15% by weight of pigment (20% for Carbon Black beads) and 28–50% resin. Time to disperse the pigment increased with increase in the amount of resin. Quick dispersion and good colour were got with 17–28% resin, if the resin content was brought to 35% before the mill was drained. Colour was judged visually under intense illumination in a box lined with black velvet, or measured by the Nigrometer or spectrophotometer. C.O.C.

Organic Coatings for Zinc Surfaces

P. Costelloe and E. Page

Bull. Inst. Met. Finishing, **8**, 107–114 (Summer 1958)

Paint finishes for zinc surfaces should be formulated on the following principles: (i) evaluation of media as both thick and thin films; (ii) use of minimal thickness of film on production articles; (iii) formulation for chromate passivation when the article must operate under arduous, e.g. tropical, conditions; (iv) wash primers not to be used on phosphated zinc surfaces; (v) maintenance of low pigment–binder ratios in primer formulations, except when formulating with inhibitive pigments of the chromate group; here the highest degree of permeability commensurate with enamel hold-out should be ensured; (vi) formulation of stoving enamels with castor alkyds where possible; (vii) with the exception of cellulose, use of non-convertible resins such as vinyl, acrylic, or chlorinated rubber types where possible; (viii) use of zinc tetrahydroxy chromate as main primer pigment where possible; and (ix) the film should be built up by successive wet coats of finishing enamel rather than with primer; this does not apply to wash primers. J.W.D.

Modern Inks and Coated Paper

G. Martin

Papeterie, **79**, 764–9 (1957): *Chem. Abs.*, **52**, 14189 (25 Aug. 1958)

A discussion of the behaviour of modern inks on coated paper. C.O.C.

Progress in Printing Inks

G. Martin

Papeterie, **79**, 363–7, 639–646, 737–740, 809–815 (1957); **80**, 31–6, 85–93, 155–163 (1958): *Chem. Abs.*, **52**, 14189 (25 Aug. 1958)

Progress made in the formulation of printing inks is reviewed under the following headings: mechanism of ink penetration and filtration (separation); composition of classical printing inks and their drying mechanism; synthetic resins in inks; composition and properties of quick-drying inks (pressure set and quickset) and high-gloss inks; use of paper in printing and common printing troubles (tinting, strike-through); composition of inks for magazine and newspaper printing, for offset, and for heliogravure and flexographic printing (aniline inks); composition and uses of recently developed heat-set, moisture-set and cold-set inks; research on development of instantaneously drying inks; inks dried by chemical means (French ultraviolet radiation dried inks and American inks hardened by SCl_2). C.O.C.

PATENTS

Rapid Setting Printing Inks

Fred'k H. Levey Co. *USP* 2,820,710

A colorant is dissolved or suspended in a vehicle consisting essentially of an alcohol-soluble cellulose nitrate containing $\not> 11{\cdot}7\%$ N, dissolved in an alkanediol of < 9 C, e.g. 2-methyl-2:4-pentadiol. This ink is rapidly set by heat, steam or liquid water and has excellent press stability. C.O.C.

Organic Ink for Use on Glass or Ceramics

Owens-Illinois Glass Co. *USP* 2,821,486

A printing ink applicable to glass or ceramics consists of a liquid epoxyhydroxy polyether resin, a pigment, citric acid as catalyst, diethylene glycol monoethyl ether and a liquid silicone. The ink should be used not before 24 hr. or later than 72 hr. after it has been made. After application it is cured at 375–475°F. for 30–10 min. C.O.C.

Hectograph Ink Vehicles

General Aniline *USP* 2,824,812

A vehicle particularly suitable in making black hectograph inks which retain their tone even after printing 150–200 copies, contains 20–35% by weight of sugar cane waxes, the remainder being other oils and waxes. C.O.C.

Coating Compositions yielding a Hammer Finish

Midland Silicones *BP* 802,342

Hammer finishes can be obtained with all known types of coating resins or polymers by using a composition made up of (1) a film-forming organic resin or polymer other than (3), (2) 0·5–100% on the weight of (1) of a metallic pigment, and (3) 0·01–2·0% on the weight of (1) of a benzene-soluble organopolysiloxane of $\not< 50{,}000$ cs. viscosity at 25°C., containing 1·99–2·01 hydrocarbon radicals per Si atom and at least half of whose polymer units are of formula R^1CH_3SiO (R^1 = aliphatic hydrocarbon of 1–3 C), the remaining units being of formula $R^2_{2n}SiO_{4-n}$ (n = 2–6; R^2 = monovalent hydrocarbons). C.O.C.

Resins for One-coat Hammer Metal Finishes

Glidden Co. *USP* 2,823,190

Heating together (1) 10–60% by weight of vinyl toluene, (2) 0·1–2·0% of divinylbenzene, and (3) an oil-modified alkyd resin made from 25–45% by weight of monocarboxylic acids of 6–24 C, and a drying or semi-drying oil yields a product which can be stored for long periods without appreciable alteration. It is particularly useful in preparing hammer metal finishes showing uniform pattern development from batch to batch. C.O.C.

Barium Borates as Preservatives for Paint Films

Buckman Laboratories *USP* 2,818,344

Addition of a Ba borate, e.g. Ba ortho-, meta-, tetra- or octaborate, to paints, particularly paints containing anatase TiO_2 (C.I. Pigment White 6) greatly improves the resistance of films formed from the paints to mildew, chalking, and collection of dirt. It also imparts increased whiteness. The susceptibility to iron staining is not increased and drying time and adhesion of the film are not adversely affected. C.O.C.

Vitreous Enamel Coatings upon Aluminium

Robertson Thain and H. H. Robertson Co. *BP* 802,832

Opaque Water Colours for Artists
A. S. Masley and H. Heyman *USP* 2,822,281

A tablet which readily disperses in water consists of pigment (10 g.), commercial ground whiting (22), acacia powder (4), starch (1), citric acid (1), 50% aq. sorbitol (5 cc.). C.O.C.

Coating with Metallic Silver
Olin Mathieson Chemical Corpn. *USP* 2,822,289

Adherent films of metallic silver are obtained on all types of non-conducting materials, e.g. glass, synthetic resins, cellulose esters, etc., by use of an aqueous ammoniacal silvering solution containing β-hydroxyethylhydrazine or a salt thereof as reducing agent. Such solutions are less susceptible to variations in working conditions than those hitherto known. C.O.C.

Improved Differential Colorimeter and its Application to the Control of Paint (XIV p. 885)

VI—FIBRES; YARNS; FABRICS

New Concept of Ultratexture of Fibrous Materials and its Experimental Basis
K. Hess

Verhandlungsber. Kolloid-Ges., **18**, 5–14 (1958): *Chem. Abs.*, **52**, 14286 (10 Sept. 1958)

An investigation of the geometric relations of lattice-oriented and unoriented synthetic high polymer cellulose and protein fibres. A cross-subdivision in micelle ropes having a band-like cross-section of approx. 40 × 60 sq. Å. is considered. The results confirm the existence of large X-ray longitudinal periods, independence of the periods of the molecular chain lengths and the lattice constitution of the crystalline phase, the representation of the periods in the electron microscope on intercalation of heavy atoms into the lattice-unoriented segments, and the bandlike formation of contrasts spread over the entire width of the fibres. C.O.C.

Influence of Capillary Forces on the Swelling of Fibres
M. Ollagnier

Chim. et Ind., **79**, 770–773 (June 1958)

The properties of liquids may be modified by the walls of capillaries containing them. It is shown thermodynamically that a liquid in a sufficiently narrow capillary cannot boil and that its surface tension may undergo large changes. When the capillary radius tends to zero the limiting pressure due to capillarity during drying equals a value which can be estimated from intermolecular forces involved. Dimensional changes in wetting and drying of cellulose fibres are interpreted in terms of capillary forces. W.R.M.

Catalysts in Photodegradation of Textile Fibres
A. Sippel

Verhandlungsber. Kolloid-Ges., **18**, 19–24 (1958): *Chem. Abs.*, **52**, 14174 (25 Aug. 1958)

Photodegradation of fibres was investigated by two methods, purely physical by measuring tear resistance and physicochemical by viscometric measurements of the change in the degree of polymerisation. The influence was determined of catalysts, e.g. TiO_2 and Fe, added to cellulose acetate on k, k^1 and m_0 values, where k = velocity constant of the decrease of resistance to tearing, k^1 = velocity constant of the decrease in degree in polymerisation, $m_0 = kk^1$. m_0 is independent of the catalyst but dependent on presence of absorbers of ultraviolet radiation. C.O.C.

Action of Bivalent Cations on Cellulose Xanthate Gels
A. Gröbe and H. Klare

Faserforsch. und Textiltech., **9**, 262–272 (July 1958)

The diffusion of bivalent cadmium ions in a cellulose xanthate gel filament is observed microscopically by following the movement of a boundary line. The dependence of diffusion on the concentrations of the cadmium ions and of acids and salts in the solutions entering the gel by diffusing is studied. Degrees of ripeness and hydration of the gel were varied. The boundary line is maintained in the cellulose hydrate form, separating two regions in the filament which behave, in dyeing, like the skin and core of a technical fibre. Theoretical aspects of the action of bivalent cations in the spinning bath on the skin and core are considered. W.R.M.

Uronic Acids of Jute Hemicellulose
H. C. Srivastava and G. A. Adams

Chem. and Ind., 920 (19 July 1958)

Three acidic components of the acid hydrolysate of jute fibres were derivatives of 4-*O*-methyl-D-glucuronic acid, in conformity with many other hemicelluloses and in contrast to the reported isolation by Das Gupta and Sarkar (*Text. Research J.*, **24**, 705 (1954)) of 3-*O*-methyl-D-glucuronic acids. A.J.

PATENTS

Regenerated Cellulose Resistant to Discolouring
American Viscose Corpn. *USP* 2,821,489

Discoloration on exposure to a hot, humid atmosphere is prevented if the fibres, film, etc. are treated with an aqueous solution containing HSO_3 ions and dried without rinsing. C.O.C.

Carbamoylethyl, Carboxyethyl and Aminoethyl Cellulose Fibres
U.S. Secretary of Agriculture *USP* 2,824,779

Cellulose textile fibres containing carbamoylethyl radicals ($-CH_2CH_2CONH_2$) and other β-substituted ethyl radicals, attached to O atoms of cellulose molecules are produced by treating cellulose fibres containing OH groups with a solution in an inert solvent of alkali, 1·0–12% by weight of hydroxide or quaternary ammonium hydroxide and 1·0–55·2% of acrylamide and then heating to cause etherification. If heating is carried out at > 100°C. for ≯ 20 min. then the reaction tends to form only carbamoylethyl cellulose ethers. The products resemble wool in their affinity for dyes, regain, insulating properties and chemical activity. C.O.C.

Light-stable Titanium Dioxide-delustred Nylon
British Nylon Spinners *BP* 802,085

The tendency of nylon containing TiO_2 to be degraded by light is reduced if the TiO_2 contains as a substituent ion sufficient vanadium, niobium, tantalum, antimony or bismuth to render the TiO_2 a controlled-valency N-semiconductor (see *Semi-Conducting Materials*, Butterworth Scientific Publications Ltd., 1951, p. 151 *et seq.*; *Chemistry of the Defect Solid State*, A. L. G. Rees (Methuen & Co. Ltd., 1954), especially pp. 12–14). C.O.C.

Enhancing the Affinity of Vinylidene Cyanide Interpolymer Fibres and Films for Disperse Dyes
B. F. Goodrich Co. *USP* 2,819,253

Acidic hydrolysation of the vinylidene cyanide interpolymer before it is formed into fibres or films much increases its affinity for disperse dyes. C.O.C.

Physicochemical and Colloidal Properties of Sols of Some Pigments used in the Mass Coloration of Viscose (IV p. 874)
Synthetic Mica (C.I. Pigment White 20) and Synthetic Asbestos (IV p. 874)

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

Non-ionic Detergents in Wool Scouring and Grease Recovery
G. Lievens and R. Bovy

Proc. 2nd Internat. Congress Surface Activity, **4**, 97–102 (1957)

Raw wool was successfully scoured with alkylphenol polyglycol detergents using counter-current circulation of the baths and low temperatures. Low residual grease contents with minimum consumption of detergent and fuel is claimed. By successive centrifuging of the liquors almost the whole of the wool grease is recoverable in a high state of purity. S.R.C.

Bleaching of Linen by the Continuous and Semi-continuous Methods
H. Pierling

Textil-Praxis, **13**, 840–843 (Aug. 1958)

The introduction of sodium chlorite has given a new impetus to the bleaching of linen fabrics. The material, in open width, is usually given an alkaline scour by impregnation at 60°C. followed by steaming, drying and batching. After washing off, the fabric is ready for impregnation with $NaClO_2$ solution, adjusted to pH 4·2 with CH_3COOH. Continuous and semi-continuous bleaching plant layouts are shown diagrammatically. L.A.T.

PATENTS

Continuous Bleaching
ICI *BP* 803,021

Cotton cloth is passed for 10–20 sec. through hot trichloroethylene or perchloroethylene. This removes 80–90% of the wax present. It is then passed through an aqueous bath at a temperature sufficient to flush off solvent contained in the cloth, desized if necessary, padded with aqueous alkali, preferably with NaOH at pH $\nless$ 10, and if desired peroxide, rapidly heated in a closed chamber with steam at 50–100°C., rinsed and, if a full bleach is desired and has not been obtained because the lye did not contain enough peroxide, padded with peroxide at pH 10–11 and again steamed. C.O.C.

Calcium and Magnesium *ortho*Phosphates as Stabilisers for Peroxide Bleaching Baths for Cotton
Becco Chemical Division, Food Machinery & Chemical Corpn. *USP* 2,820,690

In the continuous bleaching of cotton with peroxide, the bleach liquor consists of hydrogen peroxide, $\nless$ 0·01 moles/l. of a water-soluble orthophosphate and a buffer to maintain pH at 9–11. Use of this solution causes no deposit on the sides of the J-box. C.O.C.

Bleaching Dicarboxylic Esters of Cellulose
Eastman Kodak Co. *USP* 2,824,097

Cellulose acetate phthalate is readily bleached by treating with dilute alkali metal permanganate and then with a reducing acid. C.O.C.

Dry-cleaning
FH *BP* 802,625

Much improved cleaning is obtained if a carboxylic amide of $>$ 11 C which may be substituted in the amide group by Alk, hydroxyalkyl or polyglycol ether group and/or a salt of an imino-ether of $>$ 11 C, an oxyethylated compound and, if desired, water, are added to the solvent used. Thus addition to 1500 kg. of heavy benzine of 1 kg. of the methosulphates of coconut oil fatty acid ethanolamide, 1 kg. of nonylphenolpolyglycol ether containing 5 ethylene oxide groups per mol., and 1 kg. water has very good cleansing action especially towards water-soluble dirt, high capacity for inhibiting the redeposition of dirt and is readily filtered. C.O.C.

VIII—DYEING

Unlevel Dyeing in Wool Velour Cloth
F. J. Parker
J.S.D.C., **74**, 693–695 (Oct. 1958)

It has been found that mechanical abrasion can be a cause of unlevelness in the dyeing of woollen cloth with anthraquinonoid acid dyes. AUTHOR

Reduction Times of Cibanone (Ciba) Dyes
P. Ulrich and F. Pfenniger
S.V.F. Fachorgan, **13**, 423–429 (July 1958)

On account of the minuteness of the particle size, the microdisperse form of the Cibanone brand of vat dyes is admirably suited for the pigment dyeing of piece goods by continuous methods, e.g. pad–steam, where high running speeds necessitate fast reduction times of the order of 30–40 sec. A photoelectric colorimeter was used in conjunction with the Dyeometer for the measurement of reduction speeds of selected vat dyes. Reduction times for the powder, micro-powder, and micro-disperse brands are presented in tabular form. L.A.T.

Dyeing of Cellulose Acetate with Disperse Dyes. VII—Comparison with their Solubility in Organic Solvents
C. L. Bird
J.S.D.C., **74**, 688–693 (Oct. 1958)

The well known parallel between the solubility of disperse dyes in certain organic solvents and their suitability for dyeing secondary cellulose acetate has been examined. It is shown that, at room temperature, a close relationship is obtained only by using a solvent containing an appreciable amount of water, e.g. 20% aqueous diethylene glycol diacetate (DEGDA). AUTHOR

Mechanism of the Adsorption of Disperse Dyes by Cellulose Acetate
C. H. Giles
J.S.D.C., **74**, 655 (Sept. 1958)

Dyeing for the Carpet Trade
W. Beal
J.S.D.C., **74**, 677–682 (Oct. 1958)

The large-scale introduction of synthetic fibres into the carpet trade has caused many dyeing problems. The way in which these problems are being overcome is reviewed together with developments which have been taking place in dyeing for all-wool pile carpets. AUTHOR

Skein Shading for Tufted Carpets
Silk and Rayon, **32**, 561 (May 1958)

There is increasing use of skein-shaded yarns in British tufted carpet manufacture; such yarns are produced by dipping the skeins incompletely in a dyebath of one colour, then dyeing the uncoloured parts in a bath of a different colour. Variation in effect is produced by varying the proportion of the skein dyed in each colour (first dipping say half or three-quarters of the skein), and skein-shaded yarns may be used together with self-coloured yarns to give three-colour effects. Three-colour effects may also be produced, by overlapping, from two dyebaths. The initial drawback of high cost due to the additional handling has been largely overcome. J.W.D.

Dyeing of Polyamide Fibres with Disperse Dyes
F. I. Sadov and L. G. Smirnova
Izvest. Vysshikh Ucheb. Zavedenii, Khim. i Khim. Tekhnol., (1), 147–156 (1958):
Chem. Abs., **52**, 15073 (10 Sept. 1958)

Study of the solubilities of two disperse dyes and their absorption by polyamide fibres shows that these properties, under various conditions, depend on the nature of the dyes, on the surface-active substances (called by the authors "par") and also on the fibre structure. All these factors influence the shape of the absorption curves and the maximum absorption value. With dyes of low solubility in water absorption depends only on the concentration of dye in the bath in presence of the dispersing agent and is independent of the volume of the bath. With water-soluble dyes absorption decreases with increase in volume of the bath, and depends also on the concentration of dye in the bath. Increase in the content of "par" in the solution causes diminution of the absorption of dye if the concentration of dye differs from that normally dissolving in 1 g. of "par". Absorption is reversible to the point when it begins to be accompanied by capillary layer formation. C.O.C.

Dyeing Acrylic Fibres and Blends with Cellulosic Fibres
H. Kellett
Text. Manuf., **84**, 313–315 (June 1958)

The dyeing of acrylic fibres in general with different classes of dye, and of blends of Acrilan and Orlon with cellulosic fibres is discussed in some detail. Courtelle closely resembles Orlon but some differences in treatment are necessitated by its tendency to generate alkalinity under high temperature steaming conditions; these are outlined. J.W.D.

Dyeing of Acrilan Acrylic Fibre
H. R. Hadfield and W. M. Sokol
J.S.D.C., **74**, 629–640 (Sept. 1958)

The methods of dyeing Acrilan are outlined, and the limitations of various classes of dyes stated. Data are presented to show how the concentration of sulphuric acid affects the handle of the fibre and the fastness properties of acid, chrome, and 2 : 1 metal-complex dyes. Generally, disperse dyes are the most satisfactory for the dyeing of Acrilan, although for specialised purposes azoic, acid, basic, chrome, metal-complex, and reactive dyes are suggested. AUTHORS.

Dyeing of the Newer Synthetic Fibres
J. G. Graham
Teinture et Apprêts, **44**, 36–42 (Feb. 1958)

A review. A.J.

Barriness of the Colour in Textile Fabrics from Synthetic Fibres
W. Friedemann
Faserforsch und Textiltech., **9**, 296–303 (July 1958)

The main causes of barriness are discussed, and methods of identifying causes are given with examples. W.R.M.

PATENTS

Comparing the Dye Affinity of Textile Fibres
West Point Manufacturing Co. *USP* 2,817,140

Small samples of different lots of fibre are chosen and dyed under identical conditions. Preferably 1 g. samples are used and dyed simultaneously in the same bath, e.g. in individual sections of a foraminous basket. The dyed and dried complexes are then individually combed by hand to parallel their fibres and are then examined by flicker photometry. To obtain consistent results it is necessary to rotate the samples as they are exposed to the flicker photometer. C.O.C.

Increasing the Strength of Light Weight Felts so that they may be Dyed in the Normal Manner
American Felt Co. *USP* 2,817,574

Felts $\not>$ 6 oz./sq.yd. are given sufficient strength to withstand normal dyeing processes by impregnating them with a latex of acrylonitrile-butadiene copolymer and drying them with heat before dyeing. The felts should pick up about 15% of their weight of the copolymer. C.O.C.

Patterned Effects by Dyeing
Bradford Dyers' Association *BP* 802,574

The textile is treated before or during dyeing with a resist agent for the dye used. Before dyeing and if desired after the application of the resist, the textile is treated locally with a swelling agent. Thus nylon fabric is treated for 30 min. at 80°c. with Albatex WSE (Ciba) and formic acid, dried, printed with a paste containing phenol, dried at 80°c. and rinsed. Finally it is dyed for 30 min. at 90°c. with Solway Blue BNS (C.I. Acid Blue 45) in a formic acid bath. The resultant fabric has locally shrunk areas of intense blue on a puckered white ground. C.O.C.

Dyeing Acrylic Fibres
Etablissements Schaeffer & Cie. *BP* 803,095

Acrylic fibres are dyed at pH 2–3 with water-soluble organic dyes in presence of cuprous ions produced by electrolysis of a cupric salt in the dyebath. Suitable apparatus is described. C.O.C.

Vari-Tone Cloth Dyeing
United Merchants & Manufacturers *USP* 2,823,092

Cloth is dyed in rope form so that it is unevenly dyed or not dyed in streaks so as to produce effects resembling "finger paintings" or "marbleised dyeings" respectively. If the cloth is then given a pleated or plissé finish the effects of both the coloration and the finish are visually emphasised. C.O.C.

Coloured Glass Fibres
Commonwealth Engineering Co. *USP* 2,824,828

The fibres are coated with aluminium which is then anodised to aluminium oxide. They are then dyed and the dyed fibres sealed preferably by giving a hot aqueous treatment to hydrate the aluminium oxide. C.O.C.

Recent Developments in the Application of Azoic Dyes (IX this page)
Printing and Dyeing of Pile Carpet (IX this page)
Adsorption at Organic Surfaces (XII p. 884)

IX—PRINTING

Recent Developments in the Application of Azoic Dyes
M. Hückel

J.S.D.C., **74**, 640–647 (Sept. 1958)

The paper is concerned with recent knowledge of impregnation with Naphtol AS and of coupling conditions. Influence of the type of alkali in the impregnation bath on the dyeings and on the rate-of-absorption curves of various coupling components is discussed. The chemistry of the coupling of azoic combinations on vegetable fibres is outlined, and practical aspects of the buffering of the developing baths are considered. The base printing style also is briefly described. AUTHOR

Progress in Tinplate Lithography
J. Matthews

Quart. J. Tin Res. Inst., 7–10 (Spring 1958)

A review. J.W.D.

Japanese Wax Paper Method for Preparation of Screen-printing Stencils
R. Künzl and S. R. Jasani

Textil-Praxis, 13, 843–844 (Aug. 1958)

In Europe and North America, where costs of direct labour are high, screen printing stencils are usually prepared by photo-chemical methods, whereas in Asiatic countries the Japanese wax paper method is chiefly employed. The procedure does not involve complicated apparatus but it is laborious and time-consuming. The authors describe various stages of the Japanese wax paper method. L.A.T.

PATENTS

Printing and Dyeing of Pile Carpet
Deep Dye Industries *USP* 2,816,811

A base member has the pattern formed upon it by free standing thin walls. These walls form leakproof receptacles for the various dye liquors needed. The carpet to be coloured is placed pile downwards upon the base member so that the pile can soak up the dye liquors in the various receptacles. The carpet is held taut and is covered by a flat rigid sheet to ensure uniform introduction of the pile into the various receptacles. Means are provided to feed dye liquor into each of the receptacles as necessary. This enables the pile to be coloured to any desired depth, even right down to the backing if desired. C.O.C.

Improving the Adhesion of Printing Inks to Polyethylene Terephthalate
ICI *BP* 802,974

The polyethylene terephthalate is treated with ozone while maintaining the surface temperature at $\not<$ 150°c.

BP 802,975

The polyethylene terephthalate is treated by either the above process, that described in *BP* 715,914, or exposure to flame for a time insufficient to cause distortion. It is then coated with an organic thermoplastic material, e.g. *N*-methoxymethylpolyhexamethylene adipamide, and then printed on, e.g. with a photogravure ink. C.O.C.

Transfer Sheets for Spirit Duplicating
Kolok Manufacturing Co. *BP* 801,186

Master copies which are cleaner to handle, less liable to smearing and deterioration, are obtained by incorporating a metallic powder, e.g. aluminium or bronze, in lamellar form in the coating composition comprising a dye or pigment dispersed in wax, mineral oil or grease. The base sheet may be of paper or be composed of an organic or synthetic or semi-synthetic condensation or polymerisation product, e.g. cellulose acetate, Terylene or regenerated cellulose film. R.A.

Dense Black Images by Direct or Spirit Process Duplication
Ditto *BP* 802,170

Copy sheets containing the diamide of thio-oxalic acid are moistened with a suitable solvent and then pressed against a master copy bearing an image formed by a Ni, Cu or Co organic sulphonate or alkane sulphate, e.g. Ni benzene mono-, di- or tri-sulphonate. The resulting copy is fast to light and storage. C.O.C.

Self-manifolding Sheet Material
Caribonum *BP* 800,733

The upper, or receptive, side of all sheets, except the top one, is coated with an aqueous emulsion of 1% phosphotungstic, phosphomolybdic, tungstic, phosphotungstic-molybdic acid or their salts containing 1–5% methylethylcellulose, together with a hygroscopic substance, e.g. glycerol, glycols or sorbitol. The inclusion of a sharp substance, e.g. barytes, pptd. $CaCO_3$, blanc fixe or mixtures of these promotes rapid colour development. If desired, tannic acid may be added to enhance the formation of an insoluble lake. The lower, active side of all sheets, except the bottom one, carries a colourless organic dyestuff derivative, e.g. a colourless base, lactone or an ether of a triphenylmethane dye. As the thin coating of phosphotungstic acid, or similar, can be applied by the simplest means, it can be applied at the printing machine. R.A.

Casein-containing Lithographic Coating
Harris-Seybold Co. *USP* 2,822,280

When using casein in lithographic coatings the time for exposure to light when preparing plates can be very greatly reduced by treating the casein with glyoxal. C.O.C.

Colour Photography
ICI *BP* 802,275

Exposed and colour developed photographic material is treated in presence of metal equipment in a bleach bath consisting of an aqueous solution of an inorganic ferricyanide, an inorganic bromide and an inorganic nitrate. There is no corrosion of the metal equipment nor any softening or swelling of the gelatin in the photographic emulsion. C.O.C.

Mordants for Acid and Direct Dyes on Film Blanks
Technicolor Corpn. *USP* 2,821,455

Very sharp prints are obtained if the mordant used is an insoluble dibiguanide metal chelate or complex, e.g. the gelatin layer of a film blank is prepared for transfer printing by treating it with an aqueous solution of an acid salt of 4:4′-diphenylmethane dibiguanidine and then with aq. $CuSO_4$. C.O.C.

Luminescent Transfer Paper
Kee Lox Manufacturing Co. *USP* 2,822,288

One of the layers in a transfer paper contains a substance which is invisible in light but becomes visible when exposed to ultraviolet radiation or some other form of radiating energy. C.O.C.

Azine Cyan Colour Formers (IV p. 875)
Modern Inks and Coated Paper (V p. 878)
Coating of Organic Polymers with Metal Oxides or Salts by use of Ionising Radiation in absence of a Binder (X p. 883)

X—SIZING AND FINISHING

Proofing of Wool against Felting
H. Jędraszczyk

Prace Inst. Włókien, Warszawa, (26), WPLiS, pp. 14 (1957): *Polish Tech. Abs.*, **30**, (2), 149 and 151 (1958)

The author compares the most important methods of proofing wool against felting. He finds that mixed dyed yarn responds best to treatment with alcohol–hydrocarbon solutions of caustic soda, whereas for undyed raw material an aqueous solution of potassium permanganate and sodium hypochlorite is to be preferred. In the case of loose wool treated on a semi-technical scale and dyed immediately afterwards with acid chrome dyes, good results are obtained. C.J.W.H.

Penetrating Power of Synthetic Resin Precondensates into Cellulosic Fabrics
R. Loss

S.F.V. Fachorgan, **15**, 429–431 (July 1958)

It is known that the sorptive capacity of cellulose is the result of the ability of liquid to fill the capillary spaces. The capillary rise can thus be used as practical indication of the penetrative ability of liquids into the fibre micelles. It is to be expected that the penetrative capacity also depends on the viscosity of the liquid. One object of the investigation was to find a relationship between the capillary rise and the viscosity of the fluid. Filter paper strips were used for capillary rise (H_{max}) measurements of 10–, 20–, and 30% precondensate solns. Their viscosity, (η_{rel}) relative to water at 20°c. was determined in an Ostwald viscometer. It was found that $H_{max} \times \eta_{rel}$ = constant. It is concluded that the control of viscosity and sorptive characteristics of resin precondensates are indispensable for reproducible results in crease-resist finishing. Types of resin precondensates investigated included urea–formaldehyde (ordinary, cyclic, and modified), melamine–urea–formaldehyde, and acrolein–formaldehyde. L.A.T.

Silicone-rubber Coated Fabrics
H. Anders

Textil-Praxis, **13**, 844–845 (Aug. 1958)

Coating of fabrics with silicone-rubber pastes and dispersions is described. Pastes are applied either by coating (excess being removed by a doctor blade), or by immersion in a bath of solvent diluted paste. Curing times and temperatures depend on the quality of finish required and can vary from 30 min. at 125°c. to a few seconds at 300°c. Fibre glass and asbestos fabrics are coated for industrial uses. Silicone-rubbers applied from dispersions require lower curing times and are more suitable for fabrics made from thermoplastic fibres. L.A.T.

Heat Treatment of Fabrics of Synthetic and Cellulose Triacetate Fibres
Joly and Guyonnet

Teinture et Apprêts, (44), 20–24 (Feb. 1958)

A review of the principles of, and methods for, the heat-setting of thermoplastic fibres. A.J.

Polyurethan Resins "Impranils"
E. Windemuth, H. Gensel, and M. Kramer

Teinture et Apprêts, (44), 43–48 (Feb. 1958)

A review of the formation and properties of polyurethans and of their use as finishing agents. A.J.

PATENTS

Mechanically-finished Resin-treated Fabric of Improved Tear Strength
American Cyanamid Co. *USP* 2,819,179

The fabric is impregnated with an aqueous dispersion containing (1) a methylolmelamine or a methylol or alkoxymethyl derivative of a diamide, formamide, urea or modified urea, and (2) a lower alkylated methylol melamine and a compound free from basic salt-forming groups and containing Alk of $>$ 6 C and one N atom to which is attached CO and a reactive H or alkylol radical. It is then partly dried, mechanically finished by heat and pressure, dried and baked. The finished fabric has much better tear strength than similar fabrics finished without addition of (2) above. C.O.C.

Mechanical Finishing of Regenerated Cellulose Fabrics
British Industrial Plastics *USP* 2,820,715

A finish fast to washing is obtained by impregnating with an aqueous solution containing a lower alkyl ether of dimethylol urea having a minimum etherification of 75% of all its methylol groups and an acid or potentially acid catalyst, at least partly drying, giving a mechanical finish and then baking. Thus viscose rayon staple fabric is impregnated with 118% of its dry weight of an 8·5% aqueous solution of the dimethyl ether of dimethylol urea, there being 0·17% of NH_4CNS in the solution, air dried at $<$ 80°c. to 10% regain, embossed at 130°c. and baked for 10 min. at 140°c. C.O.C.

Pleated Finish
Apponaug Co. *USP* 2,817,468

The fabric is passed through a bath containing a resinous precondensate, dried to 8–15% regain and then passed through a pleating apparatus which imparts warpwise pleats. It is then pressed, e.g. by rollers, and the resin cured. C.O.C.

Epoxy Resins and Polyalkyleneimines for Reducing the Felting Properties of Wool
U.S. Secretary of Agriculture *USP* 2,817,602

Wool treated with an epoxy resin and a polyalkyleneimine and cured at 50–100°c. has its felting properties greatly reduced. The finish is resistant to hot water and laundering. The treated wool is not deleteriously affected, in particular its tensile strength and handle remain unaffected. C.O.C.

Antistatic Finish Fast to Washing and Drycleaning
DuP *USP* 2,820,724

The material is treated with an aqueous dispersion or solution of a cross-linkable oxygen-containing polyamide, a catalyst and a non-cross-linking polyether, e.g. *N*-methoxymethyl poly-4-oxaheptamethylene adipamide, citric acid and the polyether obtained by polymerising 1:2-propylene oxide to mol.wt. 1700 and then graft polymerising with ethylene oxide to mol.wt. of 2200 to obtain a product in which 20% of the ether units are derived from the ethylene oxide. C.O.C.

Water-resistant or Repellent Finish
AB. Vapor *BP* 802,187

Water-absorbing organic material containing OH groups is treated with an organic polymer after having been treated with a substance which is a catalyst for the polymerisation of the organic polymer and has affinity for the OH group of the material being treated. Thus cellulose is treated for 0·1–100·0 sec. with BF_3 at 0·01–1·0 atm., preferably 0·1 atm. Excess BF_3 is removed and the cellulose immediately treated with *iso*butylene at 0·1–10·0 atm., preferably at 1 atm. Within a few minutes the *iso*butylene polymerises with a large decrease in pressure. The material is then neutralised, preferably with ammonia or a tertiary amine. C.O.C.

Antistatic Finish
FH *BP* 802,150

Accumulation of static electricity on hydrophobic fibres is prevented by impregnating them with a solution or dispersion of a condensate of a polyvinyl alcohol of average mol.wt. of $\nless$ 10,000 and an aldehyde containing at least one sulphonic acid group, e.g. butyraldehyde sulphonic acid. C.O.C.

Water-repellent Finish
Davies-Young Soap Co. *USP* 2,820,719

The fabric is first given an antistatic finish by treating it with a solution in petroleum naphtha of a quaternary ammonium compound which does not render the fabric readily wettable, e.g. *N*-soya-*N*-ethylmorpholinium ethosulphate. After this it is treated with a petroleum solvent containing a resin and wax. C.O.C.

Applying Siloxanes to Fabrics
Midland Silicones *BP* 802,540

Siloxanes are preferentially adsorbed on the surface of the fabric when the fabric is immersed in an aqueous emulsion of the siloxanes containing a non-ionic emulsifying agent and 0·2–8·0% (on wt. of siloxanes) of a polyimine of formula $Z(CHR^1{\cdot}CH_2{\cdot}NH)_x(CHR^1{\cdot}CH_2Z)$ ($Z = NH_2$ or Hal; $R^1 = H$ or CH_3; $x > 3$), e.g. $H_2N(CH_2CH_2NH)_4H$, or a compound of formula—

$$HO\left[\begin{array}{c} NR^2_3Y \\ \dot{C}H_2 \\ H_2\dot{C}CHO \end{array}\right]_n H$$

(R^2 = aliphatic hydrocarbon of < 5 C; Y = anion; $n > 1$), e.g. $HO{\cdot}[CH_2{\cdot}CH(CH_2{\cdot}N(CH_3)_3Cl)]_x{\cdot}H$. C.O.C.

Water-repellent Finish
M.dland Silicones *BP* 803,055

An organic textile is rendered water-repellent by treating it with a 0·5–10·0% by weight solution in an organic solvent of a composition made up of (1) 15–50% by weight of a hydrolysable compound of formula $Ti(OR^{\cdot})_4$ or an aliphatic hydrocarbon-soluble partial hydrolysate thereof ($R^{\cdot}$ = aliphatic hydrocarbon of < 20 C or a hydroxylated hydrocarbon radical of < 20 C and containing < 4 hydroxyl groups); (2) 5–70% by weight of a resin formed of trimethyl siloxane and SiO_2 units so that CH_3:Si::1–2:1, and (3) 15–80% by weight of a compound of formula $R^2{}_{2n}SiO_{2-n}$ (R^2 = Alk or alkenyl of < 4 C or monocyclic; n has average value of 1·0–1·45; each Si atom has $\nless$ 1 of the R^2 groups attached to it). C.O.C.

Organo-silicon Halide Aerosols for Imparting Water Repellency to Cellulosic Materials
E. Robbart *USP* 2,824,778

Cellulosic material is rendered water repellent by exposing it to a gaseous mixture of an organic silicon halide for 1–60 sec. and an inert gas at 70–100°F. and then treating with mild alkali. Thus muslin was exposed to an aerosol of G E Dripfilm (General Electric Co.) (a mixture of methyl chlorosilanes consisting mostly of methyl trichlor and dimethyl dichloro silanes) and then treated with conc. aq. Na_2CO_3 at 100°F., rinsed and dried. The treated muslin was water repellent and retained $\nless$ 90% of its original tensile strength. C.O.C.

Hydrolysing Cyanoethylated Cotton
American Cyanamid Co. *USP* 2,820,691

By hydrolysing cyanoethylated cotton in two steps, using (1) basic hydrogen peroxide then (2) mild acidic conditions, a good degree of hydrolysis is obtained without excessive swelling. Thus cyanoethylated cotton cloth (3·2% N content) (67 parts) is treated with 35% H_2O_2 (130) diluted with water (to 375). Conc. NH_4OH(12) is then added and the reaction allowed to proceed with no attempt at cooling, until the temperature reaches 80°C. The mixture is then cooled and allowed to stand at 35°C. until the reaction is completed. The cloth is then washed with water, then with 0·1N-HCl and treated at 60°C. with 2N-HCl until maximum hydrolysis of $CONH_2$ to COOH group occurs without much hydrolysis of other parts of the molecule. The cloth is then washed well past neutral with water. When dry it contains 1·59% N and 0·69 molar equivalent of carboxyethyl groups per g. The treated cloth has high moisture regain and readily dissolves in dil. NaOH. C.O.C.

Preventing Nylon from Discolouring on being Heated
Rohm & Haas Co. *USP* 2,823,033

Treating with urea, biuret, dicyandiamide, or NH_4 cyanate so as to deposit $\nless$ 5% by weight and then heating to $\nless$ 240°F. prevents nylon from discolouring on being baked during resin finishing, or on being hot embossed or ironed.

USP 2,823,034

The same effect is obtained by treating the nylon in an aqueous solution of $\nless$ 15% by weight of one of the above compounds at 90–150°C. C.O.C.

Non-woven Fabric
Chicopee Manufacturing Corpn. *USP* 2,820,716

A carded lap has a powdered bonding material distributed throughout the dry web in a pattern covering areas of the web at regular intervals. The binder is then softened and pressure applied to fuse the softened binder together with the fibres and cause it to penetrate into the web.

USP 2,823,142

Fabric suitable for outerwear and resistant to repeated washing and dry cleaning is obtained by treating a carded loop with a thermosetting resin and a soft acrylate polymer or copolymer and then heat curing. C.O.C.

Coating Fabric with an Alkoxy End Blocked Polysiloxane
Union Carbide Corpn. *USP* 2,815,300

Flexible, tack-free products are obtained by impregnating fabric with a low mol.wt. soluble liquid polysiloxane containing end-blockers of the alkoxy type and then curing. C.O.C.

Coating of Organic Polymers with Metal Oxides or Salts by use of Ionising Radiation in absence of a Binder
DuP *BP* 802,620

The organic polymer is given a coating of $\nless 2\times10^{-6}$ g./sq.cm. of the inorganic metal compound. It is then subjected to ionising radiation of $\nless$ 0·1 m.e.v. for $\nless$ 0·01 watt-sec./sq.cm. The resultant coating has excellent fastness to washing, solvents and mechanical abrasion. The process has numerous uses on textiles, films or moulded articles. Thus it may be used on textiles to effect softness, resilience, tendency to shrink, static propensity, dyeability, pilling, hydrophilicity, etc. On films it may be used to improve adhesion of printing inks, lacquers, etc.

BP 802,621

Ionising radiation of 15–50,000 e.v. is used. C.O.C.

Decorative Cushion Fabric
Kendall Co. *USP* 2,817,597

Fabric is coated with foamed latex which is then gelled and the sponge rubber formed cured. Before final vulcanisation the rubber layer is embossed. An outer coating, e.g. of synthetic resin or paint, is applied to the raised portions of the rubber either before or after final vulcanisation. C.O.C.

Heat Stabilisation of Polyethylene Cloth
Reeves Brothers *USP* 2,821,457

Oriented polyethylene filaments are incompletely annealed so as to leave them with predetermined residual shrinkage. They are then formed into fabric and, while under tension to prevent shrinkage, heated close to but below the m.p. of the polyethylene. C.O.C.

Dodecyl Alcohol and Dodecylamine Acetate for rendering Fabrics, Cordage, etc. Rodent Repellent
Armour & Co. *USP* 2,822,295–6

Fabric, cordage, etc. impregnated with dodecyl alcohol or dodecylamine acetate repels rodents so that they neither approach it nor attempt to gnaw it. C.O.C.

Rendering Garments Shape-retaining and Water-repellent
R. Koehlert *BP* 802,222

After being ironed or pressed the garment is sprayed with an organic-solvent solution of a water-repellent substance, e.g. stearic acid anhydride or Al oleate in trichloroethylene or CCl_4, and then heated for $\ngtr$ 2 hr. at 90–140°C. C.O.C.

Continuous Rapid Pleating of Fabric (I p. 870)
Regenerated Cellulose Resistant to Discolouring (VI p. 879)
Carbamoylethyl, Carboxyethyl, and Aminoethyl Cellulose Fibres (VI p. 879)
Vari-Tone Cloth Dyeing (VIII p. 881)

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Protecting Oxidised Cellulose Fibres from Alkali Attack
G. Machell
Silk and Rayon, **32**, 525–529 (May 1958)

The formation of oxycelluloses and their subsequent breakdown by alkalis is discussed in detail. Alkali attack follows from the presence of –CHO or –CO groups; the former may be converted to –COOH by oxidation under carefully controlled conditions with chlorous acid, and the original oxidation process may be reversed by the powerful reducing action of sodium borohydride. Both methods have proved effective in the stabilisation of all types of oxycellulose, but the disposal of –CO groups remains a difficulty; work is being directed to the solution of this problem. J.W.D.

PATENTS

Sheets of Filaments of Fungi
Institute of Paper Chemistry *USP* 2,811,442

A highly flexible, high gloss sheet is prepared by the usual paper-making methods and machines from a suspension of cellulose fibres containing more than 10% by weight of filaments of fungi. The writing and printing properties of the product are comparable with those of conventional paper. The sheet is flameproof. By the action of heat and pressure the sheet may be rendered practically transparent. R.A.

Mineral-coated Paper
Rohm & Haas *BP* 802,039

Viscosity troubles encountered with known coating compositions are overcome by using copolymers of one or more lower alkyl acrylates (2·5–7% by wt. of copolymer) with itaconic, aconitic, maleic, fumaric, the dimer or trimer of methacrylic acid, as a binder for the finely divided pigmentary material. For each 100 pts. by wt. of pigment, the coating contains 8–25 pt. copolymer having a T_i value < 20°c., preferably between − 10°c. and + 10°c. The coated product is receptive to single or multi-colour inks and may be over-coated, after printing, with wax, lacquer, etc. R.A.

Sized Paper
Hercules Powder Co. *BP* 802,356

Non-water repellent paper, showing high resistance to penetration by water, ink, etc. is prepared by impregnating the web with a stable, aqueous emulsion containing a dimer of a mono-alkyl ketene of 6–20 C. The new sizing agents are 20–50 times as efficient as conventional agents, e.g. rosin size, and it is, therefore, generally sufficient to incorporate 0·05–0·2% of the agent based on the weight of pulp, depending upon the degree of sizing required. R.A.

Sizing Carbonate-filled Paper
Hercules Powder Co. *BP* 802,357

Difficulties encountered in the sizing of carbonate-filled papers, caused by their alkalinity, are overcome by use of size comprising a mineral pigment, an adhesive and a ketene dimer of formula $[RCH{=}C{=}O]_2$ (R = Alk of > 7 C; *cyclo*alkyl of > 5 C; Ar, aralkyl or alkaryl). 0·02–2% of the ketene dimer, based on the combined dry weights of pigment and adhesive, is mixed with a conventional starch or clay coating mixture. Sizing is developed on drying and curing the coated sheet. R.A.

Drum-finishing Coated Paper
S. D. Warren Co. *USP* 2,810,966

Wrinkling, curling, and uneven shrinkage in the web occur when a wet adhesive coating is dried on the paper while the web is in contact with a heated Cr-plated drum (as described in *USP* 1,719,166). This is overcome by holding the web firmly in contact with the finishing drum by means of a pressure roller having a soft, yielding surface, e.g. rubber, to a straight release line when the web is spontaneously released from the drum across the entire width of the web. R.A.

Polynitriles as Plasticisers for Cellulose Esters
Eastman Kodak Co. *USP* 2,819,979

Polynitriles of structure $NC(CH_2)_nCN$ (n > 1), e.g. succinonitrile, not only plasticise cellulose esters but also improve their toughness, flexibility, elongation, and resistance to water. They are resistant to acids and alkalies. C.O.C.

Moisture-proof Paper and Paperboard
Patent & Licensing Corpn. *BP* 800,750

The paper or board is coated with an emulsion comprising water, a microcrystalline wax, solid poly*iso*butylene or polyethylene, kaolin or ball clay as emulsifying agent, and a cationic surface-active agent as promoter. The polymer and a minor proportion of the wax are mixed to form a master batch which is mixed with the remainder of the wax. To this is added the clay–water slip and the cationic agent and the mixture is diluted with water. The polymer should be present in a proportion of 5–45% of the combined weight of polymer and wax and the ratio of combined wax and polymer should be 3–10 parts per part of clay. R.A.

Organic Copper Compounds for Stabilising Cellulose Ester Plastics to Weathering
Eastman Kodak Co. *USP* 2,819,978

Copper phenolate, copper *N*-phenyl glycinate and copper 2:5-dihydroxy terephthalate are compatible with cellulose ester plastics, are fungicides and particularly efficient as light stabilisers. C.O.C.

Modern Inks and Coated Paper (V p. 878)
Coating with Metallic Silver (V p. 879)
Regenerated Cellulose Resistant to Discolouring (VI p. 879)
Coating of Organic Polymers with Metal Oxides or Salts by use of Ionising Radiation in absence of a Binder (X p. 883)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Adsorption at Organic Surfaces

III—Constitution of Chitin and its Adsorption of Inorganic and Organic Acids from Aqueous Solution
C. H. Giles, A. S. A. Hassan, M. Laidlaw, and R. V. R. Subramanian
J.S.D.C., **74**, 647–654 (Sept. 1958)

Adsorption of mineral and organic acids, from aqueous solution, by chitin prepared from the carapace of *Nephrops norvegicus* has been studied. Full elementary analyses suggest that chitin does not consist entirely of poly-*N*-acetylglucosamine as usually supposed, but that about one-eighth of the amino groups are unacetylated. The material appears to be highly crystalline. Mineral acid anions are adsorbed at all the acetamido or amino groups of the substrate at pH about 2·5. At pH < 2·5 very greatly increased adsorption occurs, much beyond stoichiometric quantities. Organic acids, both aliphatic and aromatic, are much less strongly adsorbed than mineral acids, and < 10% of the total amount of the substrate appears to be accessible to them. Two opposing factors appear to determine the amount of an organic acid adsorbed at moderate acidities: (*a*) the crystallinity of the substrate, and (*b*) the length of the conjugate chain of the anion. The main source of anion affinity under acid conditions appears to be physical attraction between the anion and the water-solvated glucosidic residues of the chitin molecular chains. Hydrogen-bond affinity appears to be weaker than the ion–ion affinity or that due to the van der Waals attraction of large aromatic anions, and does not appear to influence the extent of adsorption under acid conditions.

IV—Adsorption of Sulphonated Azo Dyes by Chitin from Aqueous Solution
C. H. Giles, A. S. A. Hassan, and R. V. R. Subramanian
Ibid., 682–688 (Oct. 1958)

Lobster-shell chitin has been used in quantitative adsorption studies with sulphonated azo dyes in aqueous solutions, mainly under acid conditions. The extent of adsorption has been correlated with the dye structures. The mechanism of adsorption appears to be largely one of physical association between the aromatic residues of the dye and the molecular chains of the chitin, hydrogen bonding in acid solutions being unimportant. When inorganic acid is present, one sulphonate group in the dye anion takes part in ion exchange with inorganic anions at the cationic centres of chitin. Additional sulphonate groups appear to remain uncombined with the substrate and to reduce the affinity of the dye. AUTHORS

Coloured Protective Groups for the Synthesis of Polypeptides
R. Schwyzer, P. Sieber, and K. Zatskó
Helv. chim. Acta, **41**, 491–498 (March 1958)
p-Phenylazo-benzyloxy-carbonyl chloride (PZ-chloride) and *p*-(*p'*-methoxyphenylazo)-benzyloxy-carbonyl chloride (MZ-chloride) are excellent crystalline stable compounds which react with the amino groups of amino acids and peptides to give orange–yellow deriv. The PZ- and MZ-groups, like the classical carbobenzoxy group, are easily removed either by hydrogenation or with HBr in glacial acetic acid. In view of chromatographic separations these new coloured protective groups afford valuable aids for the synthesis and isolation of polypeptides.
H.H.H.

XIII—RUBBER; RESINS; PLASTICS

Reaction of Hydroxylamine and Polyacrylonitrile in Aqueous Medium
F. Schouteden
Chim. et Ind., **79**, 749–756 (June 1958)
Hydroxylamine reacts with polyacrylonitrile, dispersed in water, converting some of the nitrile groups to amidoxime groups, which react rapidly with water to form hydroxamic acid groups. Infrared absorption data are in agreement with the reactions suggested, and hydroxamic acid groups can be shown by hydrolysis and potentiometric titration of the hydroxylamine and ammonia formed. The kinetic constants for the primary reaction have been determined between 50° and 75°C.
W.R.M.

Properties of Polyamides with Siloxane Groups
V. V. Korshak, P. M. Frunze, D. N. Andreev, and É. V. Kukharskaya
J. Gen. Chem. U.S.S.R., **28**, 1997–1998 (July 1958)
The preparation of polyamides from reaction of different aliphatic or aromatic diamines with dicarboxylic acids, containing the $-Si(R_1R_2)-O-Si(R_1R_2)-$ grouping ($R_1 = R_2 = CH_3$; $R_1 = R_2 = C_2H_5$; or $R_1 = CH_3$, $R_2 = C_2H_5$), and of mixed polyamides from a mixture of adipic acid, and one of the above dicarboxylic acids with hexamethylene diamine has been carried out. The introduction of the siloxane bond imparts rubber-like properties to the polyamide and lowers its temp. of melting. G.J.K.

Synthesis of *N*-Alkyl Derivatives of Hexamethylenediamine and their Polycondensation
A. L. Klebanskiĭ and M. S. Vilesova

V—Mechanism of the Reductive Alkylation of Hexamethylenediamine
J. Gen. Chem. U.S.S.R., **28**, 1767–1772 (July 1958)
The reductive alkylation of hexamethylenediamine by its hydrogenation in the presence of butyraldehyde is investigated and although the I.R. spectrum shows the presence of some Schiff's Base (which is rapidly hydrogenated), the process is explained in terms of the hydrogenation of the diamine and interacting carbonyl compound separately absorbed on adjacent sites of the catalyst.

VI—Synthesis of Polyamides from *N*-Alkylated Hexamethylenediamine. Preparation of partially *N*-Alkylated Polyamides
Ibid., 1772–1776
The preparation and characterisation of polyamides with a varying degree of *N*-substitution has been carried out on the basis of the reaction of *N,N'*-di-, and *N*-mono-*iso*propyl hexamethylenediamine and adipic acid. The increase in the degree of substitution increases the solubility, lowers the temp. of melting and decreases the "brittleness" of the polymer. The regularity of substitution on the nitrogen in the polyamide improves the properties of the polymer more effectively compared with irregular substitution.

VII—Fully Substituted *N*-Alkylated Polyamides and their Coupling with Diisocyanates
Ibid., 1777–1781
The preparation of *N*-alkylated polyamides with different substituents has been carried out; branching substituents (*iso*propyl-, butyl-2-) produce material of a waxy nature which, after treatment with di-*iso*cyanate, is converted to a brittle solid. On the other hand, linear substituents (*n*-propyl-, or *n*-butyl-) produce material of a balsam-like character (soluble in benzene) which, under the action of di-*iso*cyanate, yields elastic products. This treatment results, irrespective of type of substituent, in increasing chain length, whereas further treatment with di-*iso*cyanate produces three-dimensional polyamides.
G.J.K.

PATENT

Pearlescent Polystyrene
Monsanto *USP* 2,817,118
Products having a pearlescent surface are produced by dissolving a solid copolymer (1–20 parts) of 95–99% *iso*butylene and 5–1% of isoprene in monomeric styrene (100), polymerising the styrene and injection moulding the resultant composition. C.O.C.

Aqueous Emulsions of Polymers for Use as Coatings, etc. (III p. 871)
Resins for One-coat Hammer Metal Finishes (V p. 878)
Coating with Metallic Silver (V p. 879)
Enhancing the Affinity of Vinylidene Cyanide Interpolymer Fibres and Films for Disperse Dyes (VI p. 879)
Improving the Adhesion of Printing Inks to Polyethylene Terephthalate (IX p. 881)
Coating of Organic Polymers with Metal Oxides or Salts by use of Ionising Radiation in absence of a Binder (X p. 883)

XIV—ANALYSIS; TESTING; APPARATUS

Quantitative Estimation of Polyethylene Oxides in presence of Fatty Alcohols
H. Etienne
Proc. 2nd Internat. Congress Surface Activity, **4**, 76–82 (1957)
Mixtures of polyglycol and fatty alcohols are frequently used as shampoo bases. The polyglycol content can be estimated by precipitation with phosphotungstic acid, independently of its mean mol.wt., followed by ashing of the precipitate. Tests on known mixtures gave adequate reliability. The influence of heavy loadings of fatty alcohols can be eliminated by the choice of suitable conditions of precipitation. S.R.C.

Subsidiary Dyes in D&C Colours
Uranine (C.I. 45350) in D&C Red No. 22 (C.I. 45380)
L. Koch
J. Assoc. Offic. Agr. Chemists, **41**, 249–250 (1958): *Chem. Abs.*, **52**, 14435 (10 Sept. 1958)
Description of a chromatic absorption method using cellulose powder (Solka-Floc SW–40A). C.O.C.

Improved Differential Colorimeter and its Application to the Control of Paint
L. G. Glasser
F.A.T.I.P.E.C. (*Fed. assoc. techniciens inds. peintures, vernis, émaux et encres imprimerie Europe continental*) *Compt. rend. 3e Congr. Spa*, 47–53 (1955): *Chem. Abs.*, **52**, 15087 (10 Sept. 1958)
Use of a ten-fold scale multiplier and other refinements has made the Colormaster colorimeter more precise than the human eye, even for colours of tristimulus values as low as 0·001. C.O.C.

Standardisation of Myrobalan Extracts for the Manufacture of Fountain Pen Inks
G. Hahn and R. A. Siddiqui
Pakistan J. Scientific & Ind. Res., **1**, 63–70 (Jan. 1958)
The chemical composition of an aq. extract of Myrobalan nuts is so complex that direct analytical methods are impracticable; standardisation is thus based on the tinctogenic value of the extract. Gallic acid is the cpd. mainly concerned in the formation of iron complexes and it was thus used in determining the optimal conditions and is used to prepare standards for the determination itself. The method and its evolution are fully described.
J.W.D.

Characterisation of Polyesters by Infrared Spectrometry
A. Giger, J. Henniker, and L. Jacqué
Chim. et Ind., **79**, 757–769 (June 1958)

Colorimetry of Fat Products
W. Weigel

Pharmazie, **11**, 786–791 (1956)

I—Fatty Acids

An account of the author's colorimetric method for determining fatty acids. The colorimetric fatty acid number indicates content of both free and combined acids and is, therefore, comparable with the saponification number; it is based on the extraction of 0·5 mg. fatty acid in a mixture of 6 ml. conc. H_2SO_4 and 0·5 ml. 10% formalin read on a layer 0·5 cm. thick with filter S43 (Pulfrich photometer). This reaction provides a quantitative determination of the total fatty acid and also a fairly precise characterisation of small amounts of fatty acids, thus avoiding the necessity for conducting preliminary identification studies (e.g. hydrolysis of fats and isolation of the fatty acids). The method is of particular value for serial comparative determination on small samples of substances.

II—Fatty Alcohols

Ibid., **12**, 357–363 (1957):
Chem. Abs., **52**, 14197 (25 Aug. 1958)

A colorimetric procedure is described for determining the total alcohols and also the saturated, unsaturated, primary, secondary, tertiary and *iso*-alcohols from propanol upwards. With complex mixture the method has advantages for serial and comparative tests over the methods at present in use. The reagent used is *p*-dimethyl-aminobenzaldehyde as a 4% solution in 50% H_2SO_4. In presence of glacial acetic acid, conc. H_2SO_4 acts on alcohols to produce unsaturated hydrocarbons through a dehydration process, the extent of the reaction depending on time and temperature. A colour test is obtained by reaction of the *p*-dimethylaminobenzaldehyde at the double bond of the hydrocarbon to produce orange to red compounds which are measured colorimetrically with a Pulfrich photometer. Use of different temperatures enables the various alcohols to be distinguished from one another. Thus with 3 ml. glacial acetic acid, 3 ml. conc. H_2SO_4 and 6·5 ml. of *p*-dimethylaminobenzaldehyde and with 10–800 γ of the alcohol at 100°c. for 1 hr., all alcohols present reacted, together with hydroxy acids and unsaturated compounds. At 60°c. for 1 hr. all unsaturated compounds reacted, as did secondary, tertiary and *iso*-alcohols branching at the β-position. At 19–21°c. for 15–30 min. and the same reagents (for lower alcohols dilute 50:50 after the reaction) only the tertiary alcohols and cholesterol reacted. (The cholesterol can be determined in other ways.) At 19–21°c. but with 5 ml. conc. H_2SO_4 and 1 ml. glacial acetic acid the unsaturated primary alcohols can be determined indirectly. With mixtures of lower and higher alcohols it is advisable to separate them into those above and those below C_{10}. The method is not applicable to propanol and butanol when mixed with alcohols of over C_5. With a mixture of homologous alcohols, a colorimetric hydroxy number (colorimetric fatty alcohol no.) can be used to determine average mol.wt. since chain length determines colour characteristics. 17 references. C.O.C.

Ultramicrodetermination of the Total Nitrogen in Polypeptides and Amino Acids isolated from Chromatograms or Electrophorograms on Paper
P. Baudet and E. Cherbuliez

Helv. chim. Acta, **40**, 1612–1620 (Oct. 1959)

The procedure, described in detail, is to heat the samples (1 to 8 μg.) in 10 μl. of eluate in sealed capillary tubes at 450°c. with sulphuric acid (1:1(v:v)) containing 0·2% mercuric chloride, the nitrogen being then determined by colorimetry with ninhydrin. H.H.H.

New Semimicro Continuous Method of Wetting Test. "Tensiometer Method" and its Applications
W. Kimura and W. Yano

Proc. 2nd Internat. Congress Surface Activity, **4**, 128–131 and 160–161 (1957)

The change of apparent density of a standard canvas or felt disc immersed in the test solution is measured with a Du Nouy tensiometer, and plotted against log time. The platinum wire ring of the tensiometer is replaced with a stainless-steel wire hook and during the test the disc is held in a vertical position by an anchor of standard weight. Only very small quantities of test solutions are required. W.K.R.

Estimation of the Average Degree of Polymerisation (DP) of Natural and Regenerated Cellulose
O. Deschler

Textil-Praxis, **13**, 835–839 (Aug. 1958)

The effect of alkalis, acids, oxidising, and reducing agents on cellulose can be ascertained by measurement of viscosity from which the average value for degree of polymerisation (DP) can be deduced. In the past various solvents have been used for this purpose, e.g. cuprammonium hydroxide (Schweizer's reagent), but light and oxygen have had to be excluded and at least 12 hr. required for complete dissolution of cellulose. Staudinger's method of nitrating cellulose and dissolving the resulting material in acetone or butyl acetate also suffers from a number of disadvantages and does not always yield consistent results. Cu-ethylene diamine (Cuene) is a very satisfactory solvent for cellulose. The material and the solvent are agitated in a stoppered flask in a mechanical shaker. Air and light need not be excluded. It was found that the time required for complete dispersion was 15 min. for regenerated cellulose and 3–4 hr. for cotton. Mercerised cotton had to be pretreated in 5% NaOH soln for 1 hr. at the boil. The specific viscosity (η_{sp}) was calculated from a formula: $\eta_{sp} = \frac{t - t_0}{t_0}$ where t_0 = time of flow of solvent, and t = time of flow of solution. The Cuene reagent has a storage life of at least 12 weeks. L.A.T.

Absolute Method for the Determination of Vegetable Matter in Scoured Wool
R. P. Harker

J. Textile Inst., **49**, T 227–T 231 (May 1958)

A sample of wool contaminated with burrs is finely divided by a rotary cutter and conditioned to a known regain. The method of separation is based on the difference in density between wool (~ 1·3) and cellulose (~ 1·5). The finely divided mixture is separated using a small, heated column of solvent of intermediate density (CCl_4 : xylene : C_2H_5OH : : 8 : 2 : 1) so that the wool floats and the burrs sink. The heat assists circulation and separation of the mixture. The wool is collected, dried and conditioned to a known regain before being weighed. A correction is made for dissolved matter from the wool— a sample of known volume is taken from the known volume of the solvent mixture used in the separation, evaporated to dryness, and the solid residue is weighed. The method is accurate to ± 0·5%. P.T.S.

Tests for distinguishing between Polyamide and Polyester Fibres
N. Bigler

Ciba Review, **11**, 30–35 (July 1958)

Analysis of Surface-active Agents by Ion-exchange Method. Rapid Semimicro Method for Determination of Anionics in the Presence of Non-ionics
S. Takahama and T. Nishida

Proc. 2nd Internat. Congress Surface Activity, **4**, 141–147 (1957)

The sample (~ 100 mg.) is dried, and the active matter is extracted by refluxing three times with 15, 10, 10 ml. *iso*propanol and filtered. The combined filtrates are diluted with 20 ml. water and passed through a column containing a cation-exchange resin (Amberlite IR-120). The column is washed with 50 ml. 50% aqueous solvent. The combined effluent is titrated with 0·05 N-NaOH (phenolphthalein). If it is necessary to employ potentiometric titration, a mixture of 1:1 96% ethanol and benzene is used as the extraction solvent. As chlorides are extracted with *iso*propanol it is necessary, if they are present, subsequently to titrate with $AgNO_3$, and apply a correction. Other common components of detergent mixtures do not interfere. W.K.R.

Identification and Determination of Verel Fibre in Fabrics
H. W. Coover, H. R. Lyon, and W. C. Wooten

Text. Research J., **28**, 530 (June 1958)

A specific qualitative test for Verel is to heat the fibre in pyridine, when it turns a deep red-brown without dissolving and colours the pyridine pale pink. The quantitative determination of Verel in blends can be made by using acetone (soluble), with, if necessary, previous washes with *cyclo*hexanone or acetic acid to remove other fibres also soluble in acetone. A value within 2% of the true value is claimed for such determinations. S.B.D.

Qualitative Test Method for Non-ionic Surface-active Agents— Cloud Number Test
Y. Tanaka

Proc. 2nd Internat. Congress Surface Activity, **4**, 132–140 (1957)

A solution of non-ionic agent in 98% ethanol or propionic acid is titrated with 2% aq. phenol to a sharp end point when the mixture becomes cloudy. Cloud No. A— for polyoxyethylene ethers is the vol. (c.c.) of phenol solution required to cloud 0·5 g. (active basis) of sample in 5 c.c. ethanol at 20°c. It varies with polyoxyethylene chain length and is characteristic of the chemical constitution. Cloud No. B— for ester type non-ionics— is the vol. (c.c.) required to cloud 0·5 g. (active basis) in 10 c.c. propionic acid at 25°c. There is a direct relationship between Cloud No. and the H.L.B. (hydrophile-lipophile balance) of non-ionics. W.K.R.

Determination of Particle-size Distributions in Suspensions from Measurements of Sedimentation Potentials
G. A. H. Elton and J. B. Peace

Proc. 2nd Internat. Congress Surface Activity, **4**, 177–182 (1957)

Particle-size distribution in heterodisperse suspensions of spherical or irregular particles of radius up to ca. 25 μ is determined by measuring the rate of change with time of the sedimentation potential developed between two levels in the suspension. Knowledge of the magnitude of the charges on the particles or the specific conductivity of the suspension is not required. The results have been shown to be in fair agreement with those obtained by microscope counting. W.K.R.

Evaluation of Detergents with special reference to Laundering
R. E. Wagg

Proc. 2nd Internat. Congress Surface Activity, **4**, 35–42 and 153–154 (1957)

Methods found to be of value in assessing the efficiency of detergents on both laboratory and plant scale are reviewed and their limitations are discussed. W.K.R.

Light Reflection in the Visible and Ultraviolet Range of Bleached Knitted Fabrics
P. I. Novodershkin

Legkaya prom., (8), 35 (1956): *Textil-Praxis*, **13**, 606–608 (June 1958)

The measurement and evaluation of the lustre number and reflection coefficient are described. Reference is made to the sensitising effect of the delustring agents in the light degradation of fibres. The author recommends increasing the twist of the yarn for dulling purposes. L.A.T.

Evaluation of Carriers for Dacron Dyeing
P. J. Scott

Amer. Dyestuff Rep., **47**, P 303–P 308 (5 May 1958)

Carriers which are toxic, carriers which degrade some fibres, and carriers which are difficult to apply are first eliminated. A certain shade is obtained with a given carrier-dye combination. The shade is matched with a second carrier and varying amounts of the same dye. The combined cost of carrier and dye is then calculated for both dyeings. P.T.S.

Dichromatism and the Mechanisms underlying Colour Vision
G. A. Fry

J. Opt. Soc. Amer., **48**, 509–512 (Aug. 1958)

Development of the writer's theory of colour-vision mechanisms, involving four photosensitive substances, for which response curves are derived from consideration of data for normal and abnormal observers. R.B.B.

Portable Telescopic Visual Colorimeter
O. E. Miller and A. J. Sant

J. Opt. Soc. Amer., **48**, 474–479 (July 1958)

A compact, portable instrument using telescopic or Maxwellian viewing. A simple colour-filter assembly is conveniently fixed to the two movable arms of a microscope stage, its position being read by the attached vernier scales. An integrating sphere and neutral wedge are incorporated. The instrument is particularly useful in some studies of colour-photography and colour-television, in which conditions may not favour the use of standard spectrophotometric techniques. R.B.B.

Mechanical Dyeing in the Laboratory
J. Wegmann

S.V.F. Fachorgan, **13**, 238–247 (May 1958)

A detailed description, with illustrations, of a Marney-type laboratory dyeing machine. L.A.T.

Age Changes in Colour Matching
J. G. Gilbert

Off. Dig. Fed. Paint Varn. Prod. Cl., **30**, 860–870 (Aug. 1958)

The Inter-society Colour Aptitude Test was given to 355 unselected subjects (180 male, 195 female) who were grouped by age and sex; the mean total scores for all colours (blue, red, green, yellow) and the mean scores for individual colours were compared.

Separate and total colour scores showed a rise from the first decade (10–19-year group) to the twenties, with a subsequent steady decline. At all ages shades of blue and green proved the more difficult to discriminate, and with these shades the ability to discriminate declined more rapidly with age. At all ages, and particularly in the sixties, wide individual differences were found in ability to match colours. Females showed an inconsistent tendency to score better than males at certain decades of life and also on certain colours. J.W.D.

Luminosity Functions for Various Field Sizes and Levels of Retinal Illuminance
R. E. Bedford and G. W. Wyszecki

J. Opt. Soc. Amer., **48**, 406–411 (June 1958)

Quite large differences are shown between the luminosity functions for four normal trichromats at field sizes 1° and below. Reverse and direct Purkinje effects are noted, according to observer and conditions. Average luminosity functions, which may be of value in photometry, should not be used in fundamental studies of visual processes. R.B.B.

Moisture Content of Samples exposed to Sunlight and in the Weather-Ometer
P. Rochas, Pierret, and Bellaton

Bull. Inst. Text. France, (73), 31–39 (April 1958)

Undyed and black dyed samples of silk, wool, cotton, rayon, and nylon fabrics were (*a*) conditioned at 20°c., 65% R.H., and (*b*) dried over P_2O_5 at 25°c. Both (*a*)- and (*b*)-treated samples were exposed in the Weather-Ometer for 20 hr. at 39°c., and the moisture contents then determined. There was little difference in moisture content (i) between (*a*)- and (*b*)-treated samples of the same fabric, and (ii) between dyed and undyed samples of the same fabric. The moisture contents of all the samples corresponded to a R.H. of 10–17% at 20°c. Tests with silk and rayon samples kept in the Weather-Ometer for 20 hr., but shielded from the arc, indicated that the true R.H. in the Weather-Ometer is in the range 40–45%. The heating effect of the radiation thus results in an equilibrium moisture content corresponding to a fictitious atmosphere at 10–17% R.H. A similar series of samples was exposed to sunlight (July, Lyons) for 5 hr. in a heliostat; 32–37°c., R.H. (shade) 18%. The moisture contents of all samples after exposure corresponded to a R.H. at 20°c. in the range 10–20%. Thus the humidity conditions in fading tests in sunlight and in the Weather-Ometer are comparable. J.C.F.

Evaluation of Metameric Colours
G. Wyszecki

J. Opt. Soc. Amer., **48**, 451–454 (July 1958)

Metameric colours are obtained in nearly all colour-reproduction work and in colour-matching procedures. Spectral reflectance curves which represent a set of colours metameric with respect to a given light source and observer may be considered as sums of a particular reflectance curve and a set of spectral reflectance curves for a series of hypothetical "metameric blacks" (for which $X = Y = Z = 0$). Tables are given of r_λ at 40 selected ordinates for a set of 37 arbitrarily defined but linearly-independent metameric blacks. Any other metameric black can be shown to be a linear combination of this independent set, which has been calculated for source "C" and the 1931 standard-observer. Thus for any given spectral reflectance curve r_λ producing tristimulus values X, Y, Z, other spectral reflectance curves may be quickly found, which produce metameric colours. R.B.B.

Diffusion Fluorimeter for Determination of the Fluorescence Spectrum of Opaque Materials
P. Rochas

Bull. Inst. Text. France, (73), 63–68 (April 1958)

An instrument is described which enables the fluorescence spectrum of opaque materials to be determined rapidly. It is primarily designed for application to textile materials containing fluorescent brightening agents. J.C.F.

Standardised Lighting Recommendations for Critical Colour Matching and Production Tinting of Paint Products
W. B. Reese

Off. Dig. Fed. Paint Varn. Prod. Cl., **30**, 522–539 (May 1958)

Colour matching *per se* should be carried out by means of North Daylight, this being a common light source of constant composition. A secondary illuminant should also be used to detect metamerism; that suggested is produced by an incandescent lamp operating at about half its rated voltage and it is termed "Horizon Sunlight". The tinting of production batches against standards should be carried out with the aid of another secondary illuminant, and that proposed is given by a mixture of lights from fluorescent and incandescent lamps, and has a colour temp. of ca. 7400°K. For the use of these secondary light-sources the surround should be of a light neutral grey of no lower reflectance than Munsell N7/(43%). The relative positions of light-source, observer, and samples must be such as to minimise or eliminate reflected glare from the sample. The above conditions are claimed to give enhanced precision in matching, elimination of metamerism, and reduced eye fatigue in the operator. J.W.D.

***L/Y* Ratios in Terms of C.I.E. Chromaticity Coordinates**
C. L. Sanders, and G. Wyszecki

J. Opt. Soc. Amer., **48**, 389–392 (June 1958)

An extension of recent studies by the above authors shows that the lightness (L)-correlation established as a second-degree equation in X, Y, Z, does not apply over a wide range of luminous reflectances. However, the ratio of lightness to luminous reflectance was satisfactorily represented by a second-degree equation—

$$L/Y = a_1x^2 + a_2y^2 + a_3xy + a_4x + a_5y + a_6$$

in the chromaticity coordinates, x and y, for 106 Munsell samples covering a large part of the gamut of existing surface colours. R.B.B.

Scope and Limits of Colour Measurement
J. W. Perry

Nature, **181**, 1704–1706 (21 June 1958)

Report of the Physical Society symposium, Imperial College, London, 2nd April 1958. Progress is discussed in the application of tolerances to colour measurement in many industries, including textiles, paint, leather, paper, colour printing, and fluorescent lighting. The various methods of colour tolerance specification depend basically on approximate or actual discrimination data and each has its supporters in particular fields of application. The narrow limits measurable may well be extended in practice by economic factors. Otherwise, effort may be wasted in attempting absolute matches, especially if the goods are sufficiently non-uniform in colour to show up when assembled or made-up into garments. In contrast, to dispense with colour-standards of doubtful permanence may require a higher accuracy than is at present possible in colorimetric specification. Fluorescent lamps can now be manufactured to a chromatic accuracy comparable with the difference in colour between the two sodium D-lines. This still leaves scope for wide variation in acceptability as a general purpose illuminant, unless some control of spectral energy distribution is specified at the same time. R.B.B.

Simple Technique for the Calibration of the Wavelength Scale of Spectrophotometers
N. V. Parthasarathy and I. Sanghi

Nature, **182**, 44 (5 July 1958)

Two absorption cells contain the same concentration of acid-base indicator (e.g. bromocresol green) but differ suitably in pH. The difference in their transmittancies at different wavelengths may be used to locate the isosbestic point of the indicator with some precision on the wavelength scale of the instrument. Comparison with published values, e.g. W. R. Brode, *J. Amer. Chem. Soc.*, **46**, 589 (1924), enables the scale to be calibrated. R.B.B.

PATENT

Testing the Impregnite Content of a Fabric
U.S. Secretary of the Army *USP* 2,819,153

Cloth impregnated with impregnite, i.e. a mustard gas deactivating agent, e.g. bis(dichlorophenyl)urea, is readily tested for impregnite content without deleteriously affecting it by applying one drop of a solvent for the impregnite, e.g. tetrachloroethane or any chlorinated benzene formed only of CH and Cl, followed by one drop of an aqueous solution containing an iodide and one-third as much of a thiosulphate which is calculated to be equivalent to the protective quantity of impregnite. A little Na dihexyl sulphosuccinate is also present in this solution. In between 2 and 10 sec. the wetted spot is tested for free I, the presence of which indicates that a protective amount of the impregnite is present. Finally the spot is neutralised with an aqueous solution of $NaHCO_3$, Na acetate, a wetting agent and Fluorescein (C.I. Acid Yellow 73). C.O.C.

Polarographic Reduction of Diazotised Aromatic Amines (IV p. 872)
Chloroplast Pigments and Chromatographic Analysis (IV p. 874)
Catalysts in Photodegradation of Textile Fibres (VI p. 879)
Comparing the Dye Affinity of Textile Fibres (VIII p. 881)

XV—MISCELLANEOUS

Effects of Certain Compounds related to Trypan Blue on the Experimental Production of Liver Cancer
K. Fujita, T. Mine, T. Ito, and M. Matsuyama

Nature, **181**, 1732–1733 (21 June 1958)

PATENTS

Providing Articles with a Pile Finish
B. B. Chemical Co. *BP* 801,333

A carrier sheet is coated with a solution of a film-forming material in a volatile organic solvent after which flock fibres are deposited on the coated sheet while it is being vigorously shaken. This ensures that most of the fibres are deposited on the film so as to form a perpendicular pile. The solvent is then evaporated off and the film with the fibres stripped off the carrier sheet. The product can then be stuck to any desired surface to provide a pile finish. C.O.C.

Corrosion Resistant Coatings of Uniform Colour on a Succession of Aluminium Articles
American Chemical Paint Co. *USP* 2,814,577

When using a mixture of fluorides, hexavalent chromium and phosphates and/or arsenates as the coating agent corrosion-resistant and decorative coatings of uniform colour and appearance on a succession of aluminium articles are obtained if maintenance of a set and definite fluoride : chromate ratio is dispensed with and if the "active fluoride" is kept constant regardless of the actual fluoride : chromate ratio. By "active fluoride" is meant the ability of the coating bath to etch a piece of lime soda glass as measured by loss in weight. C.O.C.

Increasing the Filling Power of Hen Feathers by Treatment with Magnesium Silicofluoride
U.S. Secretary of the Army *USP* 2,821,456

Treatment with a 1% aq. $MgSiF_6$ brings the filling power of hen feathers up to that of duck feathers. Feathers which have been dry cleaned are treated at 55–60°C. while dirty feathers are treated at up to 100°C. C.O.C.

Black Oxide Coatings on Steel and Iron
I. L. Newell and E. A. Walen *USP* 2,817,610

Addition of Na thiocyanate, thiourea or an alkyl thiourea, to a conventional oxidising bath used to produce a black coating on steel prevents deposition of a copper smut on the steel and maintains the blackening efficiency of the solution. C.O.C.

FORTHCOMING MEETINGS OF THE SOCIETY — *continued from page* viii

— continued from page viii

Thursday, 26th February 1959

WEST RIDING SECTION. *Fast Shades on Wool-Cellulose Unions.* D. R. Lemin, Esq., B.Sc. (Imperial Chemical Industries Ltd.). Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 6th March 1959

LONDON SECTION. *The Use of Antistatic Agents in Textile Processing.* A. E. Henshall, Esq., B.Sc. (Imperial Chemical Industries Ltd.). The Royal Society, Burlington House, **London W.1.** 6 p.m.

MIDLANDS SECTION. Section Annual Dinner. George Hotel, **Nottingham.**

Tuesday, 10th March 1959

LEEDS JUNIOR BRANCH. *New Methods for the Assessment of Dyeing Properties and Usability of Dyes.* G. H. Lister, Esq., B.Sc., Ph.D. Lecture Theatre, Department of Colour Chemistry and Dyeing, The University, **Leeds.** 3.15 p.m.

NORTHERN IRELAND SECTION. *Stenter Drying.* T. A. Uthwatt, Esq., B.A., A.M.I.E.E., and J. S. Woollatt, Esq., B.Sc. (Mather & Platt Ltd.). Grosvenor Rooms, **Belfast.** 7.30 p.m.

SCOTTISH SECTION. Annual General Meeting. 7 p.m. Followed by *Modern Cloth Drying Principles and Machines.* K. S. Laurie, Esq., A.M.I.Mech.E., A.M.I.E.E. (John Dalglish & Sons Ltd.). St. Enoch Hotel, **Glasgow.** 7·15 p.m.

Wednesday, 11th March 1959

SCOTTISH JUNIOR BRANCH. Annual General Meeting 7 p.m. *Dyeing Unions Containing Acrylic Fibres.* B. Kramrisch, Esq., F.R.I.C., F.T.I., F.S.D.C. (Ciba Clayton Ltd.). Technical College, **Paisley.** 7.30 p.m.

Thursday, 12th March 1959

BRADFORD JUNIOR BRANCH. *Sizing Materials— Their Chemistry and Application.* J. H. MacGregor, Esq., Ph.D., F.R.I.C., F.C.S. (Courtaulds Ltd.). Institute of Technology, **Bradford.** 7.15 p.m.

MIDLANDS SECTION. *Dyeing and the Future.* J. Boulton, Esq., M.Sc.Tech., F.R.I.C., F.T.I., F.S.D.C., President of the Society. (Joint meeting with the Coventry Textile Society.) Courtauld's Acetate and Synthetic Fibres Laboratory, Lockhurst Lane, **Coventry.** 7 p.m.

SCOTTISH SECTION. *The Reactivity of Keratin.* Professor J. B. Speakman, D.Sc., F.R.I.C., F.T.I., F.S.D.C. Scottish Woollen Technical College, **Galashiels.** 7.30 p.m.

WEST RIDING SECTION. *The Sorption of Moisture by Fibre-forming Polymers.* L. Valentine, Esq., B.Sc., Ph.D. (Tootal Broadhurst Lee Co. Ltd.). Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Saturday, 14th March 1959

BRADFORD JUNIOR BRANCH. Annual General Meeting. Institute of Technology, **Bradford.** 10.15 a.m.

Tuesday, 17th March 1959

HUDDERSFIELD SECTION. *Fast Shades on Wool-Cellulose Unions. Recent Advances in this Field.* D. R. Lemin, Esq., B.Sc. (Imperial Chemical Industries Ltd.). Silvios Cafe, **Huddersfield.** 7.30 p.m.

Wednesday, 18th March 1959

MIDLANDS SECTION. *Photoelectric Colorimeters . . . their uses and limitations in the Dyehouse.* J. V. Alderson, Esq., B.Sc., A.R.C.S. (Joint meeting with the British Association of Chemists.) Midland Hotel, **Derby.** 7 p.m.

Thursday, 19th March 1959

MANCHESTER JUNIOR BRANCH. Films— *Silk. Principles of Chromatography. How the World Looks to a Colour Defective,* Room J/B 16 — Chemical Engineering Building (Jackson Street), College of Science and Technology, **Manchester.** 4.30 p.m.

Friday, 20th March 1959

MANCHESTER SECTION. *Symposium on Re-active Dyes.* College of Science and Technology, **Manchester.** Further details later.

Thursday, 2nd April 1959

MIDLANDS SECTION. *Colour Physics and Match Prediction.* (Lecturer to be announced later.) (Joint meeting with the Textile Institute.) Carpet Trades Ltd. Canteen, **Kidderminster.** 7 p.m.

Friday, 3rd April 1959

LONDON SECTION. *Recent Developments in Dyeing.* T. Vickerstaff, Esq., M.Sc., Ph.D., F.S.D.C. (Imperial Chemical Industries Ltd.). George Hotel, **Luton.** 7 p.m.

Thursday, 9th April 1959

WEST RIDING SECTION. Annual General Meeting. Colour Film on *How the World Looks to a Colour-defective.* Victoria Hotel, Bridge Street, **Bradford.** 1

Friday, 10th April 1959

The Society's Annual General Meeting and Dinner, Grand Hotel, **Leicester.**

Wednesday, 15th April 1959

MIDLANDS SECTION. Annual General Meeting of the Section followed by a showing of New Scientific Films. King's Head Hotel, **Loughborough.** 7 p.m.

Thursday, 16th April 1959

MANCHESTER JUNIOR BRANCH. Three short papers by members of the section. Room J/B 16 — Chemical Engineering Building (Jackson Street), College of Science and Technology, **Manchester.** 4.30 p.m.

Friday, 17th April 1959

MANCHESTER SECTION. Annual General Meeting. *Stenter Drying.* A. T. Uthwatt, Esq. (Mather & Platt Ltd., Research Dept.). The Textile Institute, **Manchester.** 7 p.m.

Tuesday, 21st April 1959

HUDDERSFIELD SECTION. Annual General Meeting. Followed by a Colour Film on *How the World Looks to a Colour-defective.* Cmdr. Dean Farnworth (United States Naval Research). Silvios Cafe, **Huddersfield.** 7.30 p.m.

Friday, 24th April 1959

LONDON SECTION. Annual General Meeting. Commander Dean Farnworth (United States Navy) will show and discuss his film *How the World Looks to a Colour-defective.* Waldorf Hotel, **London W.C.2.** 6 p.m.

APPOINTMENTS

Advertisements relating to APPOINTMENTS VACANT, APPOINTMENTS WANTED, and MISCELLANEOUS ITEMS are invited for insertion on this page. Advertisements of Appointments Wanted are gratis to members, but must not exceed twenty-four words.

All inquiries relating to Advertisements should be addressed to THE GENERAL SECRETARY, THE SOCIETY of DYERS and COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE.

Replies may be addressed Box —, THE SOCIETY of DYERS and COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE, where all communications relating to these Advertisements are treated in strict confidence.

APPOINTMENTS VACANT

A WELL-ESTABLISHED expanding Textile Engineering Firm has a vacancy for a Technical Representative to be based in the Northern half of England. Knowledge of the Textile Industry and wet-processing of fibres an advantage but not essential. Car provided. Write giving full personal details in confidence to Box V160.

COLOMBO PLAN
DIRECTOR OF JUTE RESEARCH—PAKISTAN

APPLICATIONS are invited for the post of DIRECTOR OF JUTE RESEARCH (TECHNOLOGY) at a newly established Jute Research Institute near Dacca, East Pakistan. Will be required to take charge of technological research on Jute and to advise the Central and Provincial Governments on matters relating to technological research on jute and other fibres. Should be preferably a physicist with experience of research in fibre technology at a Textile Research Institute in this country. Full knowledge of jute technology essential. Salary £3,000 p.a. (subject to U.K. income tax) plus *tax-free* oversea allowance of £1,400 p.a. (married) or £860 p.a. (single) and other allowances. Furnished accommodation for married man provided. Duration two years in the first instance. Contract with the U.K. Government. For further information and application forms write Ministry of Labour and National Service (E.9), Almack House, King Street, London S.W.1, quoting A12/PAK/163/TCS.

CHEMISTS

BRITISH NYLON SPINNERS LIMITED require CHEMISTS for their expanding Research and Textile Development Departments. A good honours degree is an essential qualification and while post-graduate experience either in industry or for a higher degree is desirable, it is not essential. Vacancies are at various levels, involving a wide range of interests, including such topics as organic synthesis, general physico-chemical work in the polymer field, the technology of the melt-spinning process, and the application of chemistry to dyeing and finishing problems. Two vacancies in particular are (1) for work on surface chemistry and emulsions; and (2) for work in a finishing laboratory on physical and chemical modifications of nylon fabrics.

Staff conditions of employment are comparable with the best obtainable in this country; facilities and equipment are provided without stint and salaries are generous and progressive. Married men need not encounter serious difficulty in resettling their families, as rented houses are available in the area and the Company gives assistance with the cost of removals.

Applications should be addressed to The Personnel Manager (Ref. T/143), British Nylon Spinners Limited, Pontypool, Mon.

WANTED—TEXTILE CHEMIST, graduate, expert on finishing processes and quality tests for a new patented world-wide finishing process. About two months training in French and German laboratories envisaged. Applications with copies of certificates, references and salary required to be sent to Mr C. A. Cheeseman, Colonial House, Mark Lane, London E.C.3.

ADDRESSES WANTED FOR RE-DIRECTION OF JOURNALS

The Journals of the Society having been returned through the post it is desired to obtain information for these to be forwarded and any assistance in this respect will be appreciated

Cameron, M. C., *formerly of* 11 Thirlmere Gardens, Belfast, N. Ireland

Ciprut, J. V., *formerly of* Technical College, Dyeing Dept., Bradford, Yorkshire

Drzewicki, M., *formerly of* Flat 2, 11 Rectory Road, West Bridgford, Nottinghamshire

Gale, R. A., *formerly of* 32 Wordsworth Street, Hapton, near Burnley, Lancashire

Harvey, H. C., *formerly of* 77 Edinburgh Road, Congleton, Cheshire

Heaton, R., *formerly of* 142 Browning Road, Manor Park, London E.12

Hubler, B., *formerly of* Park Hotel, Oak Avenue, Manningham, Bradford 8

Jackson, J. B., *formerly of* 36 Arden Road, Crumpsall, Manchester 8

Jliadis, S., *formerly of* Nottingham and District Technical College, Shakespeare Street, Nottingham

Kothawala, Amin A., *formerly of* 36 Briarwood Drive, Wibsey, Bradford 6

Kubba, S., *formerly of* 10 Malone Road, Belfast, N. Ireland

Le Bek, I. A. G., *formerly of* 8 Lad-Hill Lane, Greenfield, near Oldham, Lancashire

Maschas, L., *formerly of* 43 St. John's Road, Huddersfield

Midgley, F. B., *formerly of* "Clova", 57 Jeremy Lane, Heckmondwike, Yorkshire

Oxley, R., *formerly of* 27 Hayling Road, Sale, Manchester

Ramadan, A. S., *formerly* c/o Beida Dyers, Dyeing Department, Alexandria, Egypt

Rahman, S. M. K., *formerly of* Look View Hall, 1025 Gt. Western Road, Glasgow

Richardson, D., *formerly of* 139 Laund Road, Salendine Nook, Huddersfield

Slater, W. K., *formerly of* 85 Hope Road, Sale, Cheshire

Smith, L., *formerly of* 80 Fair View Road, Bacup, Lancashire

Troxler, M. D., *formerly of* Georgia Institute of Technology, Box 680, Ga. Tech., Atlanta, U.S.A.

Tsien, P. C., *formerly of* 1332 Tenan Road, Shanghai, China

Wahba, F. S., *formerly* c/o Beida Dyers S.A.E., P.O. Bag., Alexandria, Egypt

Wailes, N. T., *formerly of* "Hamewith", 4 Kingsway Terrace, Dundee, Scotland

Walker, T. H., *formerly of* J. L. Stifel & Sons Inc., 339 Main Street, Wheeling, W. Va., U.S.A.

Zwicky, A. M., *formerly of* 23 West Leight Street, Crumpsall, Manchester 9

NEW MEMBERS

Persons desirous of joining the Society as Ordinary Members or Junior Members can obtain Application Forms from the General Secretary, or from the Honorary Secretary of any Section of the Society

Crawford, J., Rylstone, 1017 Burnley Road, Loveclough, Rossendale, Lancashire

Crone, H. H., 24 Craigielea Crescent, Milngavie, Dunbartonshire

Dadabhoy, M. A., 9 St. Andrew's Street, Blackburn, Lancashire

Dawson, T. W., Kelsall & Kemp (Tas) Ltd., G.P.O. Box 413, Mayne Street, Launceston, Tasmania

Dennison, A. N., 37 Lyndhurst Gardens, Ballygomartin Road, Belfast

Hampshire, D., Courtaulds (Aust.) Ltd., Tomago, N.S.W., Australia

Haworth, S. (Miss), Croasdale, Woodgate Road, Billinge End, Blackburn

Heslinga, F. J. M., Bevrijdingsplein 15, Leiden, Holland

Hill, B., British Cotton & Wool Dyers Assn. Ltd., 22 Cumberland Street, Manchester 3

Holden, J., Whitefield, 16 Alderley Road, Wilmslow, Cheshire

Hoyles, A., 14 Eastbury Avenue, Horton Bank Top, Bradford 6

Huang, S. Y., 6 Chatham Court, 2nd Fl., Kowloon, Hong Kong

Mannion, K. F., British Cotton & Wool Dyers Assn. Ltd., 22 Cumberland Street, Manchester 3

McKeand, A. H., 21 Sandy Lane, Accrington, Lancashire

Newton, E. J., 10 Mitchell Avenue, Halstead, Essex

Redfern, A. G., 6 Princess Street, Dukinfield, Cheshire

Regan, T. J., The British Cotton & Wool Dyers Assn. Ltd., 22 Cumberland Street, Manchester

Sidlow, R., 8 Pearson Row, Worthinghead Road, Wyke, Bradford

Re-admission of Member

Balmforth, D., Dept. of Colour Chemistry & Dyeing, The University, Leeds 2

MEMBERS' CHANGES OF ADDRESS

Brough, M., *formerly of* 15 Crackenedge Lane, Dewsbury, Yorkshire, *to* 11 Park Street, Crackenedge Lane, Dewsbury, Yorkshire

Desai, B. R., *formerly of* J. K. Cotton Mills Ltd., L. Kamlapaj Road, Kanpur, India, *to* Pulgaon Cotton Mills Ltd., Pulgaon (Waldha Dist.), India

Hulme, Wm., *formerly of* 1787 Leclerc Street, Sherbrooke, Quebec, Canada, *to* 17 Scott Road, Prestwich, Manchester

Kitson, D. L., *formerly of* 163 Soothill Road, Batley, Yorkshire, *to* 31 Clarke Road, Isipingo Beach, Natal, South Africa

Stevenson, M. C., *formerly of* Blackbrook House, Blackbrook, Belper, *to* 2 Friarsfield, Burleigh Drive, Duffield Road, Derby

Warren, J. F. D., *formerly of* 62 Shanklin Drive, Nuneaton, Warwickshire, *to* 1 Postern Terrace, Town Street, Duffield, Derbyshire

Weir, J. R. M., *formerly of* 549 Brown Terrace, Carron Road, Falkirk, Stirlingshire, *to* 12 Haugh Street, Carron Road, Falkirk, Stirlingshire

Wilson, L. R. H., *formerly of* Park House, Rufford Park, Yeadon, Yorkshire, *to* Beech Court, Apperley Lane, Apperley Bridge, near Bradford

Wood, F., *formerly of* 54 Catherine Street, Keighley, Yorkshire, *to* 50 Springfield Road, Baildon, near Shipley

Wright, J. C., *formerly of* 13 Greystone Avenue, Leicester, *to* 21 Wimborne Road, Leicester

Younger, K. D., *formerly of* 14 Dragon Parade, Harrogate, Yorkshire, *to* 7 St. Clair Street, Otley, Yorkshire

Zavaglia, E. A., *formerly of* 59 Fillmore Street, Phillipsburg, New Jersey, U.S.A., *to* 20 West Delaware Avenue, Newark, Delaware, U.S.A.

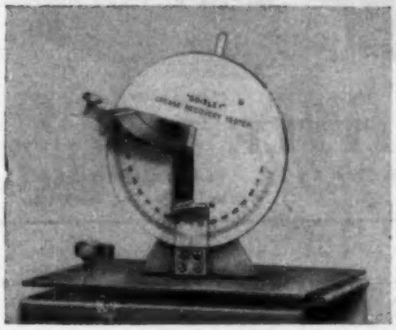
JOURNALS WANTED

The Society is urgently wanting Journals (in good condition) for January, February, March, April, May, June and August 1888, September 1955, January, February, March and November 1956, also January 1957.

Please address communications to the General Secretary

FINISHERS

Crease Recovery



The effect of crease resist finishes on cotton, rayon and other fabrics can be quickly and accurately measured with the "SHIRLEY" Crease Recovery Tester. This instrument is easy to use and gives a direct reading of the crease recovery in degrees.

Indispensable for quality control work and ensuring that standards are being maintained.

Please send for leaflet SDL/3bY

SHIRLEY DEVELOPMENTS LIMITED

40 King Street West · Manchester 3

Telephone DEAnsgate 5926 and 8182

THE SOCIETY OF DYERS AND COLOURISTS

The ANNUAL GENERAL MEETING and DINNER

will be held at

THE GRAND HOTEL LEICESTER

on

Friday 10 April 1959

DERBY AND DISTRICT COLLEGE OF TECHNOLOGY

Special Lecture Course

on

RECENT ADVANCES IN TEXTILE DYEING AND FINISHING TECHNOLOGY

Spring Term Session 1958-59

Particulars obtainable from the course organiser

D. C. COLINESE B.Sc A.R.I.C

INDEX TO ADVERTISERS

PUBLISHED BY THE SOCIETY OF DYERS AND COLOURISTS AND PRINTED BY CHORLEY AND PICKERSGILL LTD LEEDS ENGLAND
ENTERED AT THE NEW YORK N.Y. U.S.A. POST OFFICE AS SECOND CLASS MATTER